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14. ABSTRACT Study has been initiated of practical synthesis and the chemistry of 1) 1,2,3,4-tetrazines and their products, 2) 5,6-disubstituted-1,2,3,4-tetrazine 1,3-di-N-oxides, 5,6-diketo-1,2,3,4-tetrazine 1,3-di-N-oxide and its derivatives, isomeric 1,2,3,4,5,6,7,8-octazanaphthalene tetroxides (DTTO and IsoDTTO), various substituted benzotetrazine 1,3-di-N-oxides and their transformations, isomeric furoxanotetrazine 1,3-di-N-oxides, furazanotetrazine 1,3-di-N-oxide, (FTDO), 5,6-(1,2,3-triazolo)-1,2,3,4-tetrazine 1,3-di-N-oxides, and various 1-nitroacetylenes and dinitroacetylenes and their respective precursors and derivatives. The various synthetic routes studied have been illustrated and discussed in part. Further studies of the above high-energy materials are proposed.					
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Synthesis of 1,2,3,4-Tetrazines, 1,2,3,4-Tetrazine Di-N-oxides, Pentazole Derivatives, Pentazine Poly-N-oxides, and Nitroacetylenes

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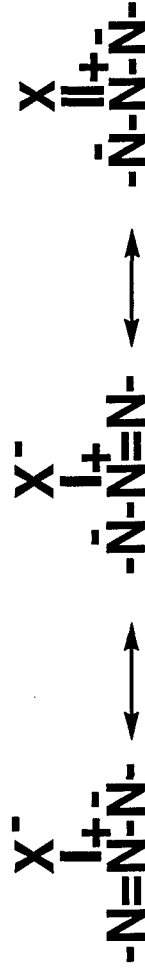
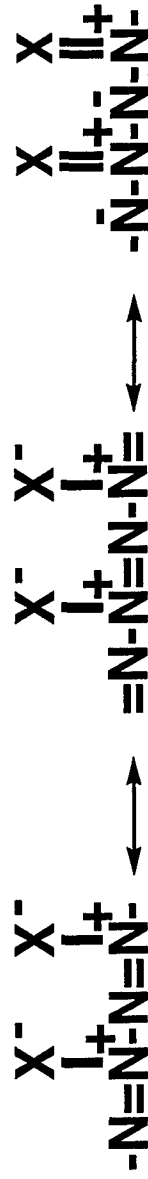
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This visual final report (September, 2005) is a summary of research on the chemistry of 1,2,3,4-tetrazines and 1,2,3,4-tetrazine di-N-oxides as published from Moscow since 1988 by many researchers in the Zelinsky Institute and as explored by Dr. M. Venugopal and Dr. D. Srinivasulu at OSU since early 2001. In this report many new and interesting structures will be considered and various approaches to synthesis of energetic molecules have been studied or will be proposed. The Russians have published over 35 experimental papers on 1,2,3,4-tetrazines since 1988; there are none from the US to date. Over 38 different authors from the Zelinsky Institute have contributed to the Russian work as presently published. The Russians have also published many important theoretical papers on 1,2,3,4-tetrazines since 1984; the US has published one theoretical paper on this subject.

Stabilized Systems Alternate Positive-Negative Charges (APNC)



X = O, NR, and CR₂

*This concept should
be extended to boron
and phosphorus
compounds!*

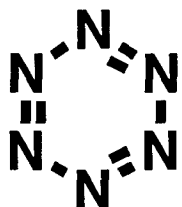
This is an important concept in considering new syntheses of high-energy materials! Menkin and Tartakovsky et al are deserving of a Nobel prize!!

Substitute NX for O
in nitrate (NO_3^-),
nitrite (NO_2^-),
pernitrate (O-O-NO_2)
and related oxygen
nitrogen compounds
(R-NO_2 , RONO ,
 RONO_2 , etc.)!

Menkin, 1988; Churakov, 1991

The concept of APNC was originated by Menkin, a theoretician in Russia, and serves as the basis for this program. The APNC ideas will be extended to many energetic molecules as yet unknown. There is much research to be done on APNC energetic materials. Most US researchers are not aware of the many Russian theoretical and experimental contributions with respect to APNC molecules.

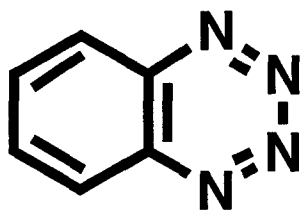
Stabilized N-Oxides



unstable

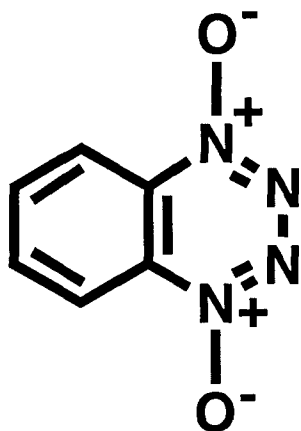
Many chemists in the 1940s tried to prepare N_6 , a benzene analog.

This molecule has not been generated previously at low temperature. Can it be prepared and used? All efforts at OSU to prepare this molecule at temperatures as low as -112°C have been unsuccessful! Physical chemists should study this molecule or its bis-diazo isomer in matrix. Is the tetrazine ring open or closed?



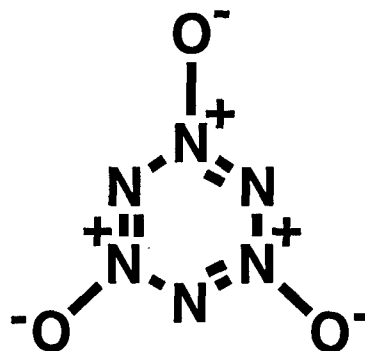
unstable

This molecule undergoes rapid loss of nitrogen to give benzyne!



unstable

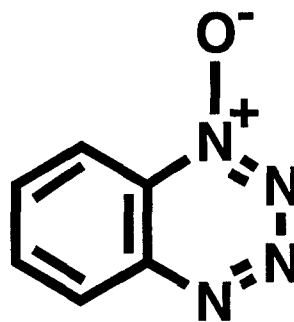
This tetrazine dioxide loses N_2 to form o-dinitrosobenzene. No one has examined this molecule at low temperatures.



life: < 1 sec

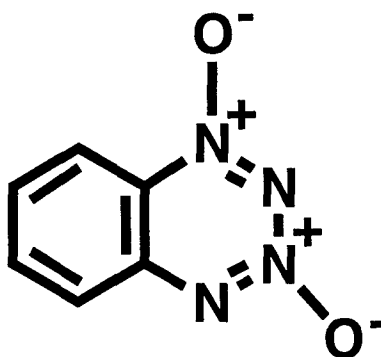
Can N_2O be polymerized or copolymerized?

Very few chemists know that this molecule, N_6O_3 , will go through a mass spectrometer! This molecule is a trimer of nitrous oxide, N_2O !



preparable

This tetrazine N-oxide melts at $72-74^\circ\text{C}$ and can be "kept" for 6-7 hours before decomposition to benzofurazan upon loss of N_2 !

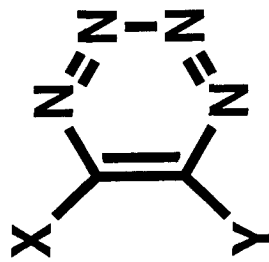


**stable,
usable**

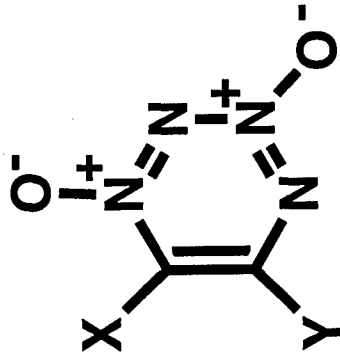
This molecule is stable, is now readily prepared, and melts at $172-174^\circ\text{C}$. OSU has improved synthesis of BTDO! A practical molecule!

The Zelinsky chemists have been studying this molecule, BTDO, since 1984. Over 36 Russians have been studying this molecule!

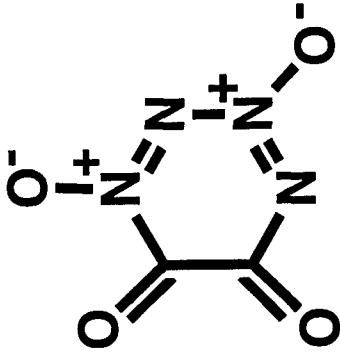
Synthesis of High-Energy Heterocycles



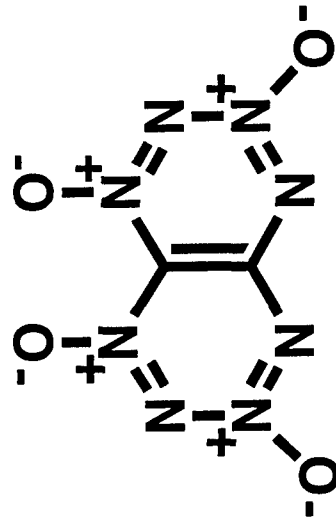
We at OSU are studying possible preparation, stability, and utility of simple 1,2,3,4-tetrazines at low temperatures. If such tetrazines can be utilized, this whole area will become very important. As yet, such 1,2,3,4-tetrazines have been found to be unstable!



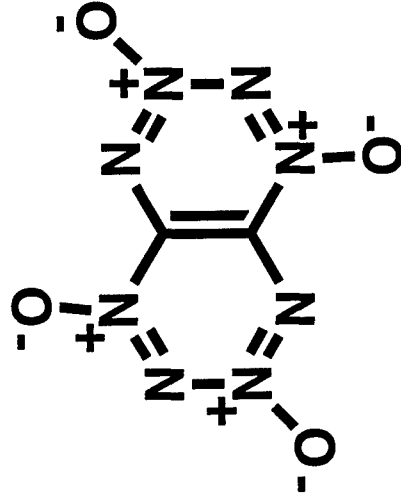
This is a major objective of the program at OSU.



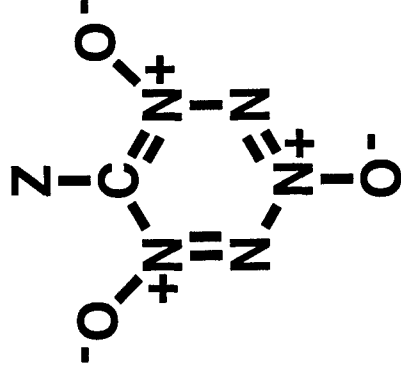
We are beginning study of synthesis of this molecule on our DARPA project.



DTTO: A very important molecule. Synthesis of DTTO is a major objective of the OSU-DARPA-Air Force research effort at OSU! The Russians are keeping their studies SECRET! See calculations!



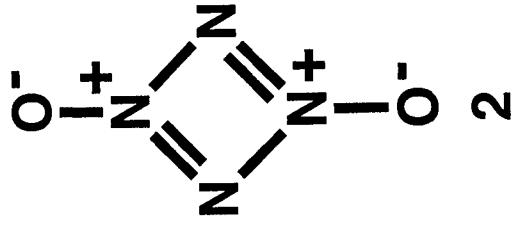
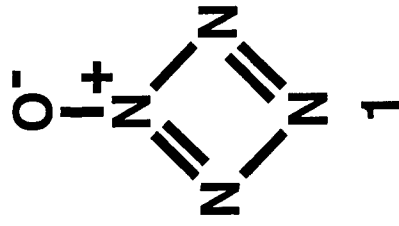
IsoDTTO: An important molecule being studied in Russia. IsoDTTO is a major objective of the program by DARPA/Air Force at OSU. See calculations in a later overhead.



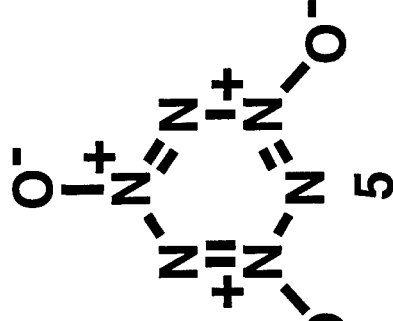
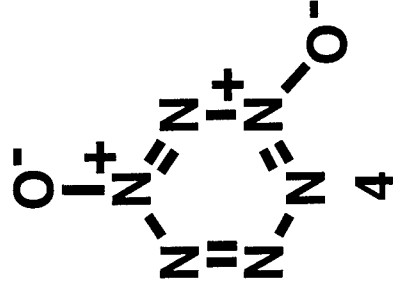
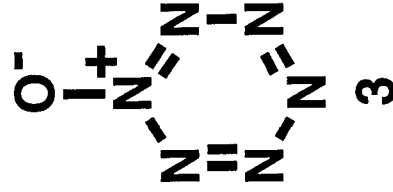
Calculations are in progress!

A very important molecule whose synthesis is being attempted at OSU. This molecule and its isomers should be excellent sources of N_2O for use in engines and combustion machines.

An unknown molecule at present. Additional funding is necessary for study of synthesis of such molecules. This research should be encouraged! A major objective!



Reactions of N_2O with catalysts and electron-transfer reagents in liquid CO_2 should be investigated. Are oligomers and polymers formed?

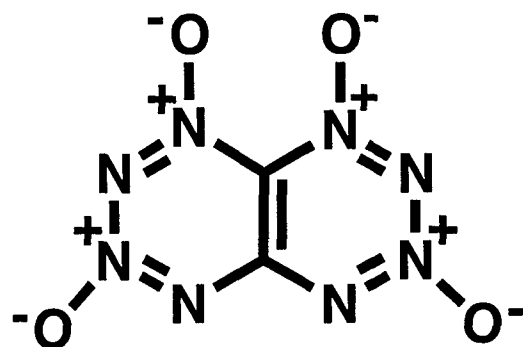


The cation-radical of **5** goes through a mass spectrometer. Menkin *et al* say that N_2O will polymerize and form stable big-ring oligomers upon activation by electron-transfer!

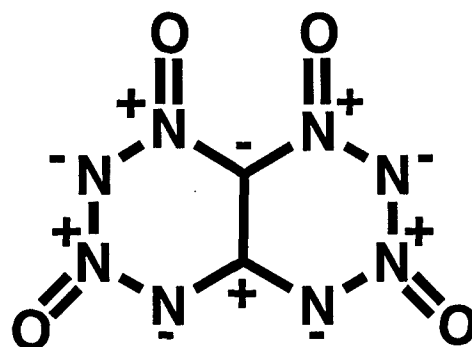
Bartlett *et al*, *J. Phys. Chem.*, 2001

Prof. R. Bartlett (Florida), upon learning of the Menkin APNC concept, calculated that **2** is more stable than **1** and that **5** is more stable than **3** and **4**. As yet **2** has not been prepared. Oligomerization, polymerization, and cycloaddition reactions of N_2O should be studied by military agencies. *Chemists study catalyzed reactions and fixation of N_2 ; they do not investigate catalyzed reactions of N_2O or N_3F !* Few know that N_2O undergoes acid-catalyzed additions to olefins and acetylenes! Such reactions were discovered in England in the 1940s and we (OSU) used these reactions in the mid 50s! *Research groups should study acid, metal-catalyzed polymerization, and electron-transfer reactions of N_2O and of N_3F !*

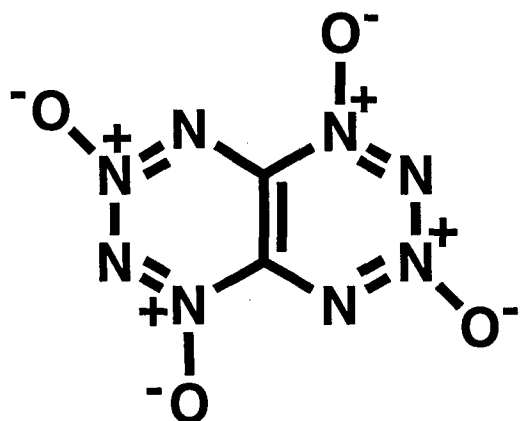
Synthesis and determination of the utility of DTTO and IsoDTTO are of major interest at OSU (Dr. M. Venugopal) and in Moscow. This project at OSU will require additional funding. The structures of DTTO and IsoDTTO are illustrated and discussed below.



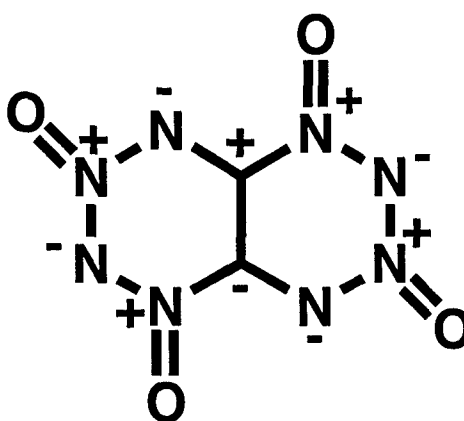
DTTO
(the more energetic isomer!)



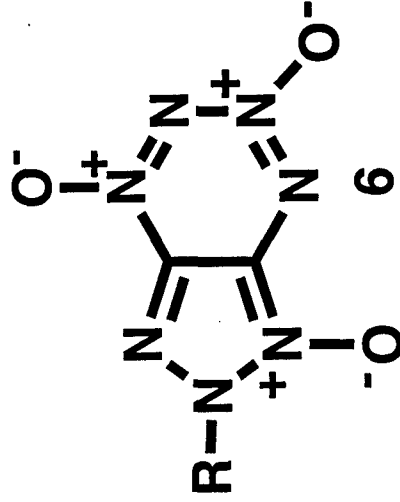
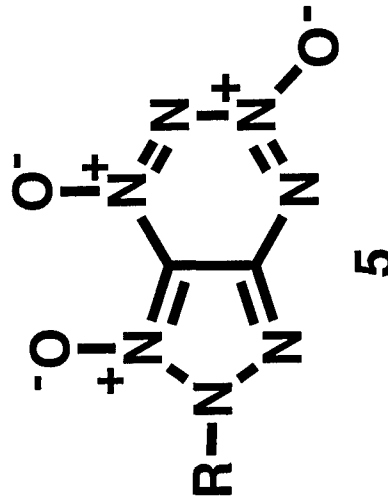
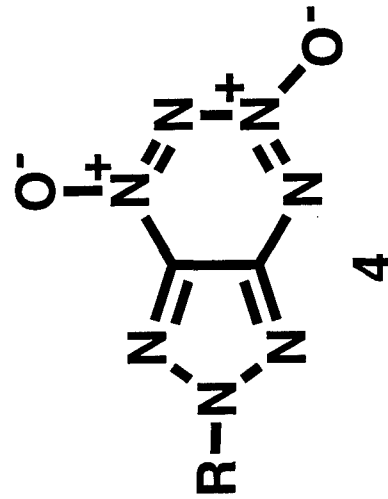
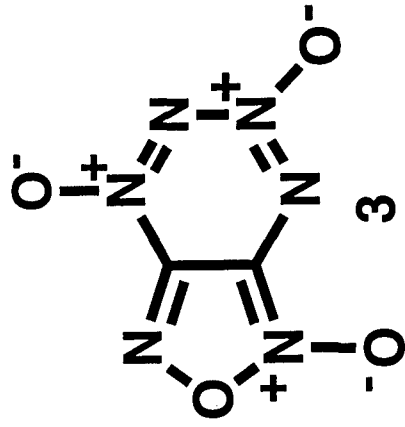
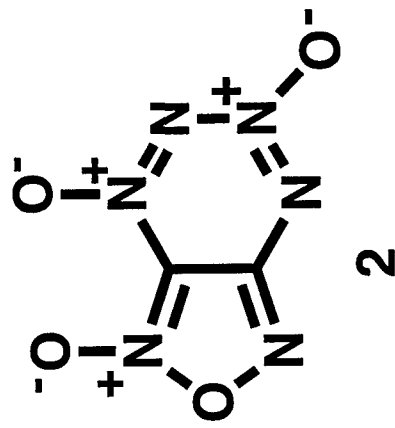
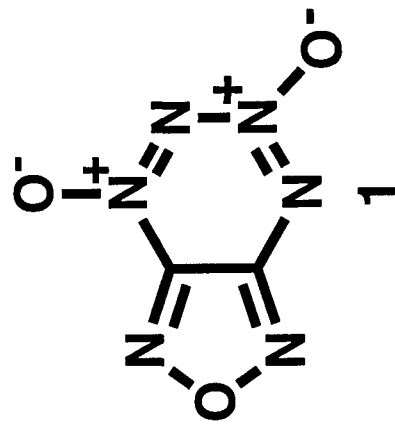
Note the alternating positive and negative charges! DTTO and IsoDTTO will have very high densities.



IsoDTTO

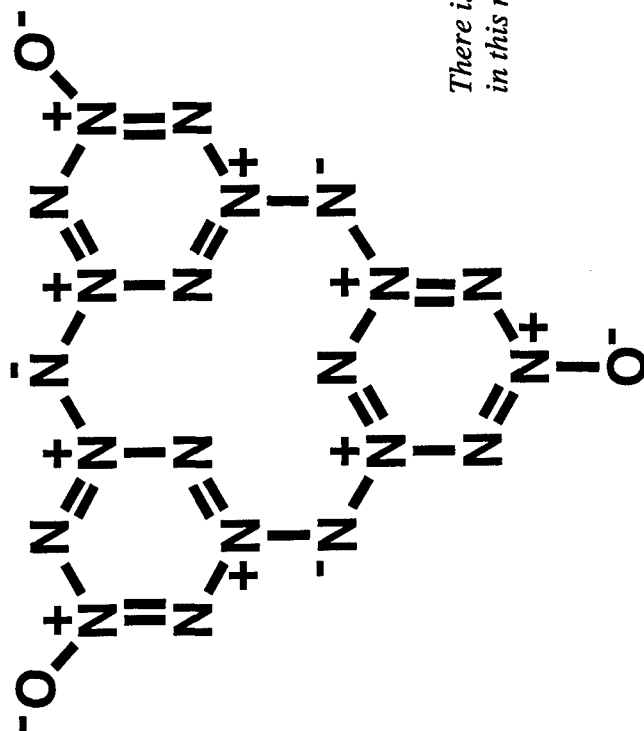
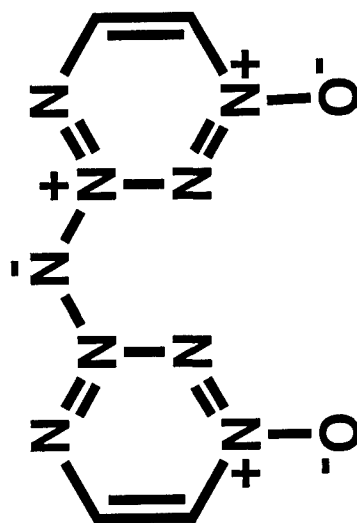
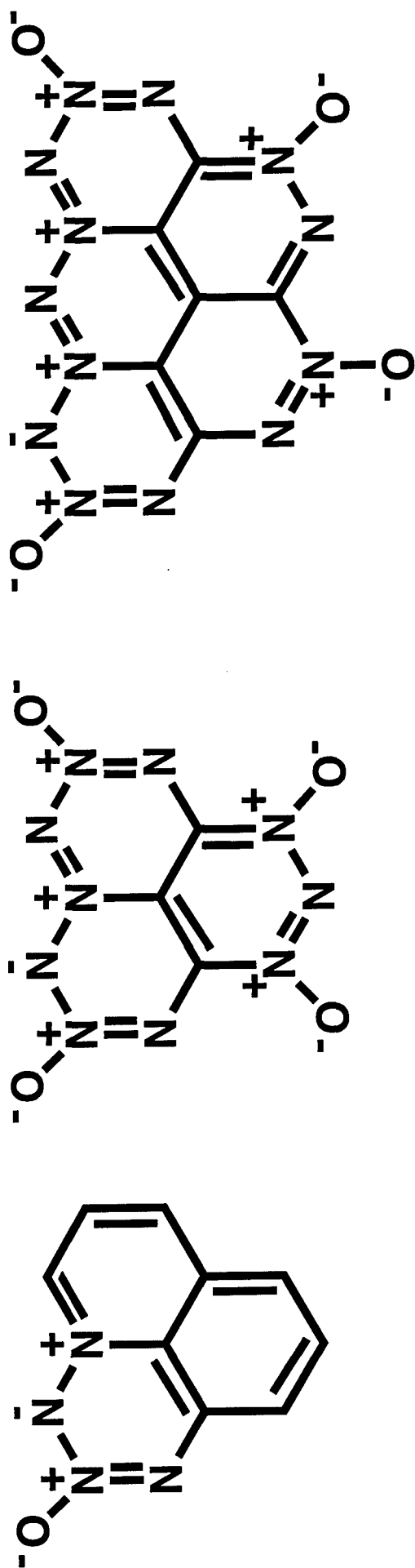


This overhead illustrates the ultimate APNC characters of DTTO and IsoDTTO. Tartakovsky emphasized the Menkin concept in his West Coast seminar in 1995! *Will these molecules ever be practical? We should make determined efforts to learn where the Russians and the Chinese are in syntheses of DTTO and IsoDTTO.* This research effort at OSU will require further support and commitment. Foreign academic post-doctoral researchers need long-term academic support in order to obtain visa stays in the US. It has not been appreciated how emotionally difficult it is for a young researcher in the US to work in an area in which we are so far behind that in Russia.



Compound 1 has been synthesized (tentative) in Moscow and at OSU. It is hoped to oxidize 1 to 2 or/and 3. As yet these efforts have not been successful. Compounds 2 and 3 are isomers of DTTO and IsoDTTO and of interest as energetics. At present we do not have good crystals of 1 for X-ray analyses. Large scale syntheses of 1 need further funding. Oxidations of 1 to 2 and/or 3 have not been successful as yet; further studies are necessary. Identifications of the structures of the hydrolysis products of 1 are in progress. Studies of syntheses of 4 and 5 have been initiated by Dr. Srinivasulu. These syntheses are also tied to advantageous preparations of dinitroacetylene! Energetics 4-6 are of major interest to OSU and to Moscow. Diaminofuroxan has been recently reported by Moscow to be unstable. The studies at OSU could not be completed by Sept. 30, 2005. This work should be discussed further with possible sponsors.

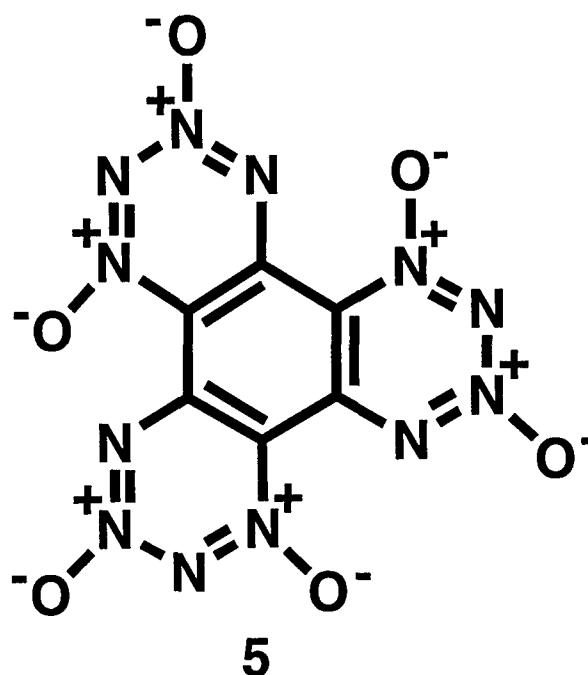
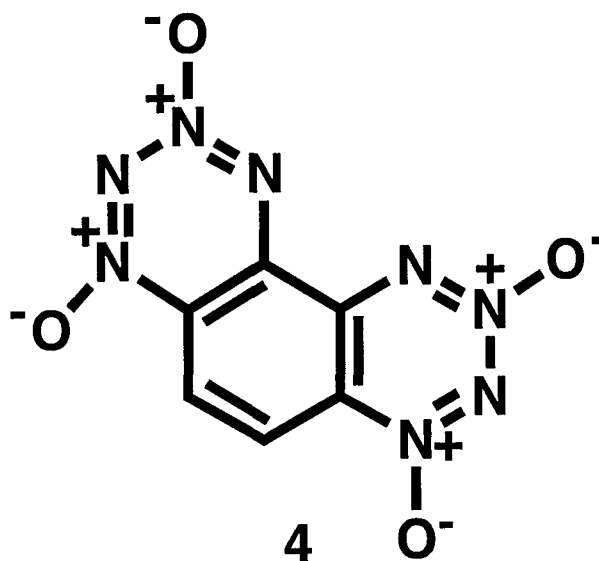
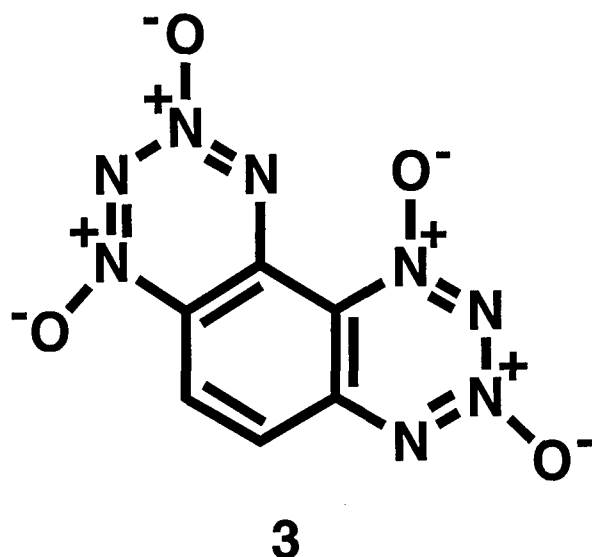
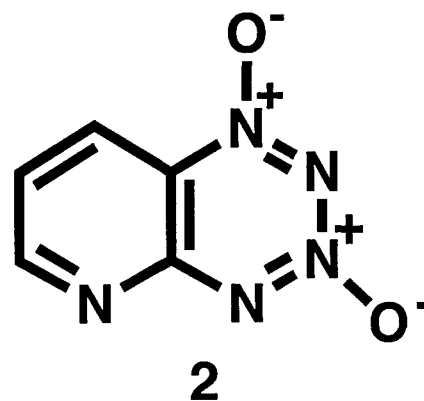
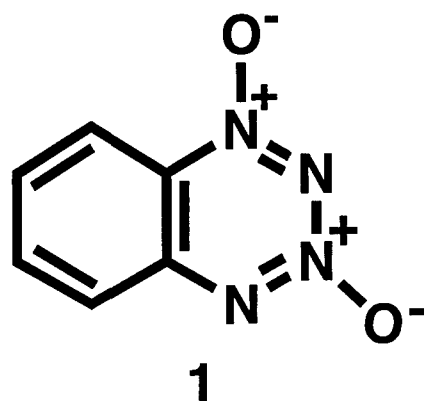
Alternating Positive-Negative Heterocycles



These molecules have been theorized by Menkin et al to be stable! These structures should stimulate future proposals for study of polymerization of N_2O , FN_3 , and other azides. Later overhauls will amplify such studies.

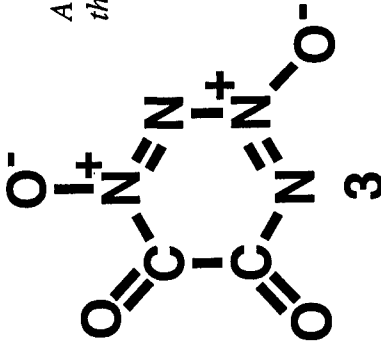
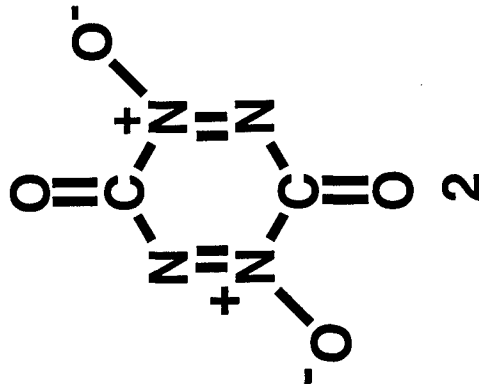
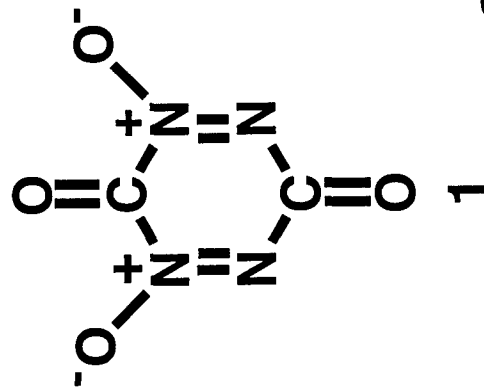
There is no carbon in this molecule!

$(N_{21}O_3^{3+})$



Compounds 1, 2, and 3 have been synthesized in Moscow. They are stable molecules. Preparation of 5 is being attempted by Zelinsky chemists. As yet, no simple 1,2,3,4-tetrazine 1,3-di-N-oxide has been reported! Such syntheses have been the main objectives of research by OSU/DARPA/Air Force investigators.

Carbon Monoxide-Nitrous Oxide Heterocycles

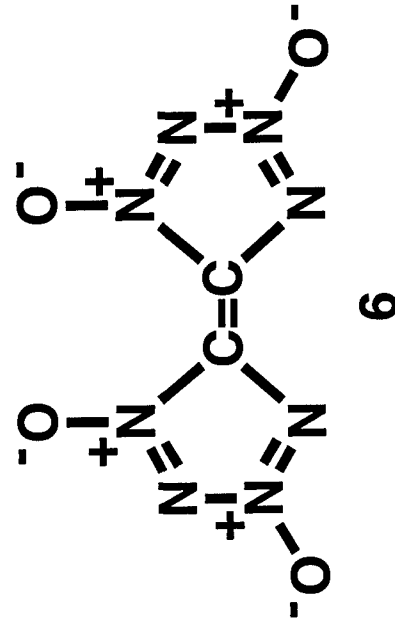
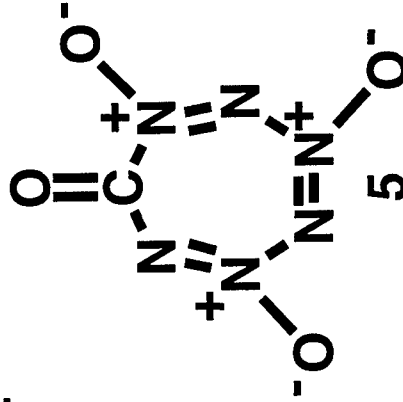
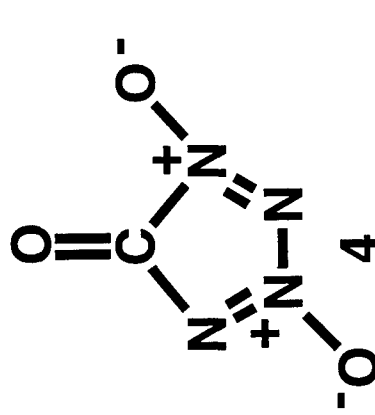


A practical molecule? Is this molecule stable?

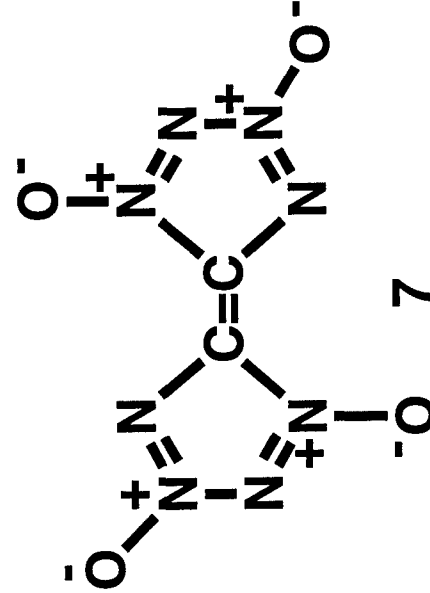
Practical molecules? Further support is necessary.

1 and 2 should be practical molecules preparable from COCl_2 and H_2NNH_2 or COCl_2 and NaN_2O .

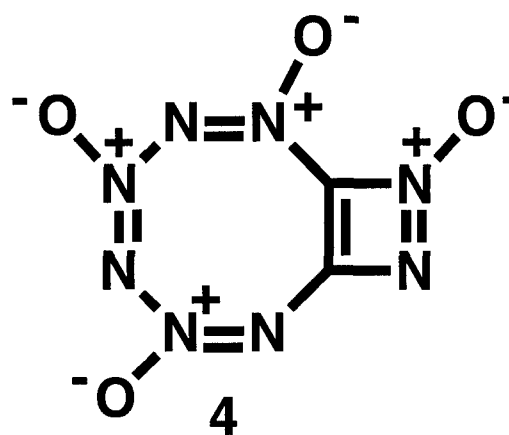
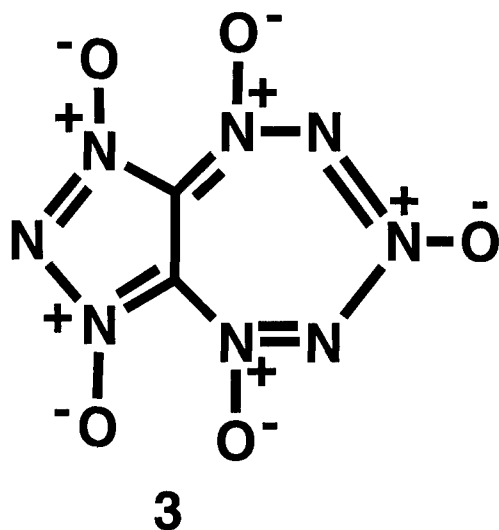
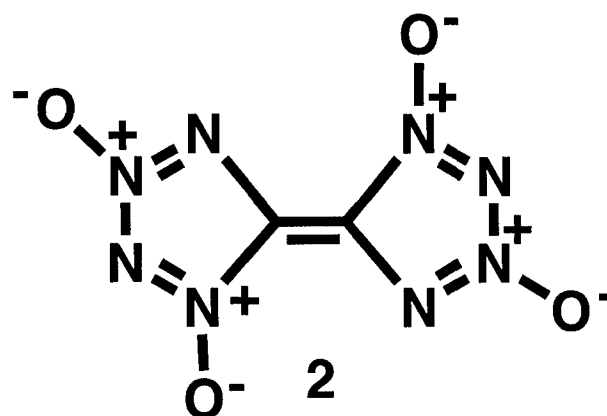
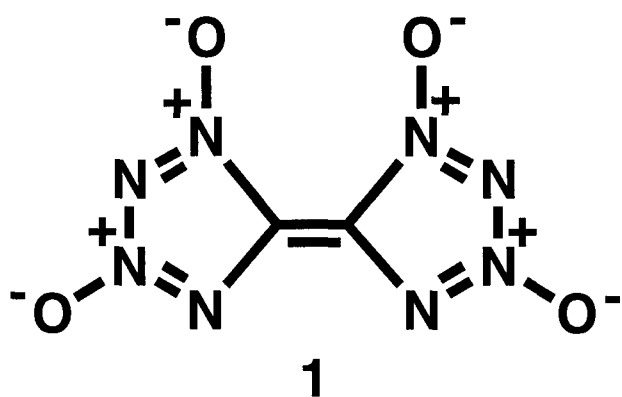
Synthesis of 3 has been investigated at OSU. Cmpd 3 may be the best possible source of DTTO and/or IsoDTTO. Cmpd 3 may also be an excellent engine fuel additive!



Are there catalyzed reactions of N_2O with CO? Many chemists are intrigued by such molecules!

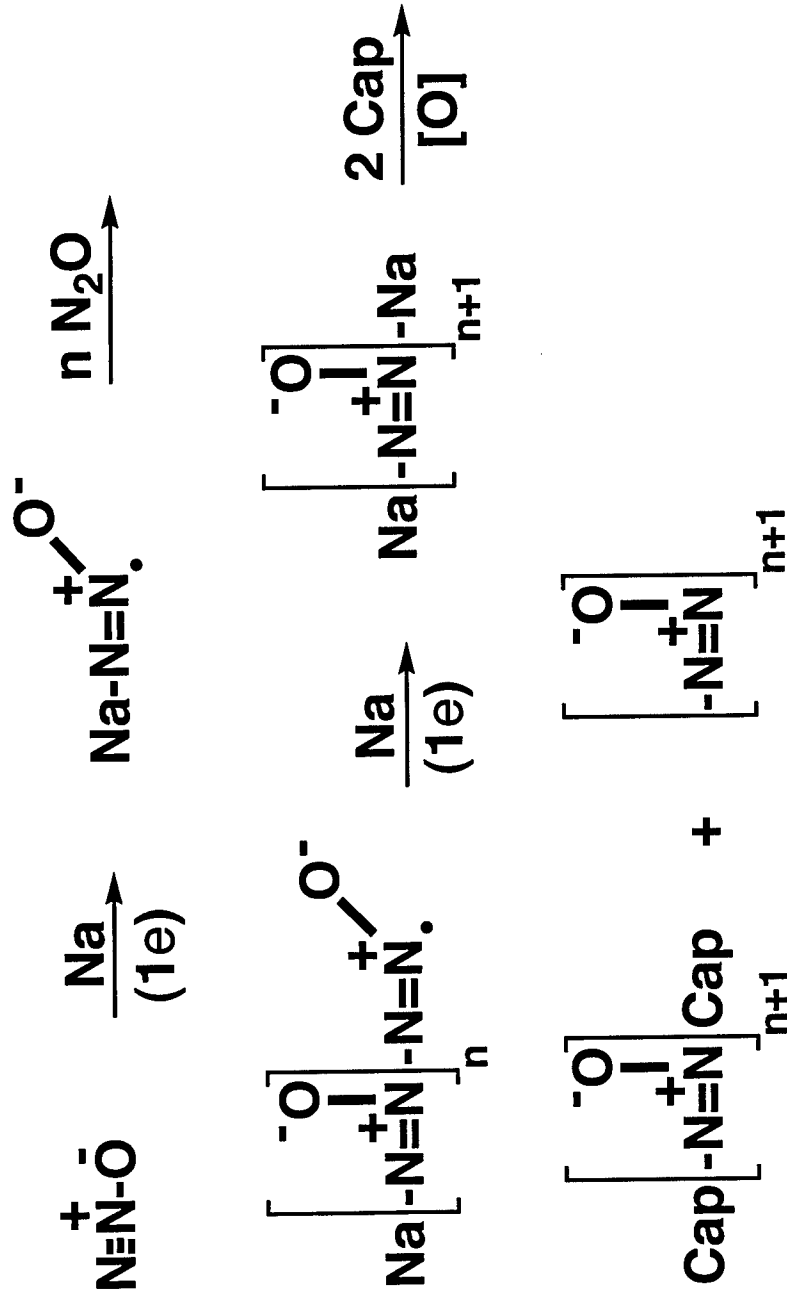


Possible energetics!



Compounds 1 and 2 are interesting energetic E- and Z- isomers which may be preparable. Calculations and the theory of the energetic molecules on overheads 10-12 are being developed. Structures 1 and 2 might be prepared simply from diazo precursors! Logical routes to such diazo precursors will be proposed to government agencies.

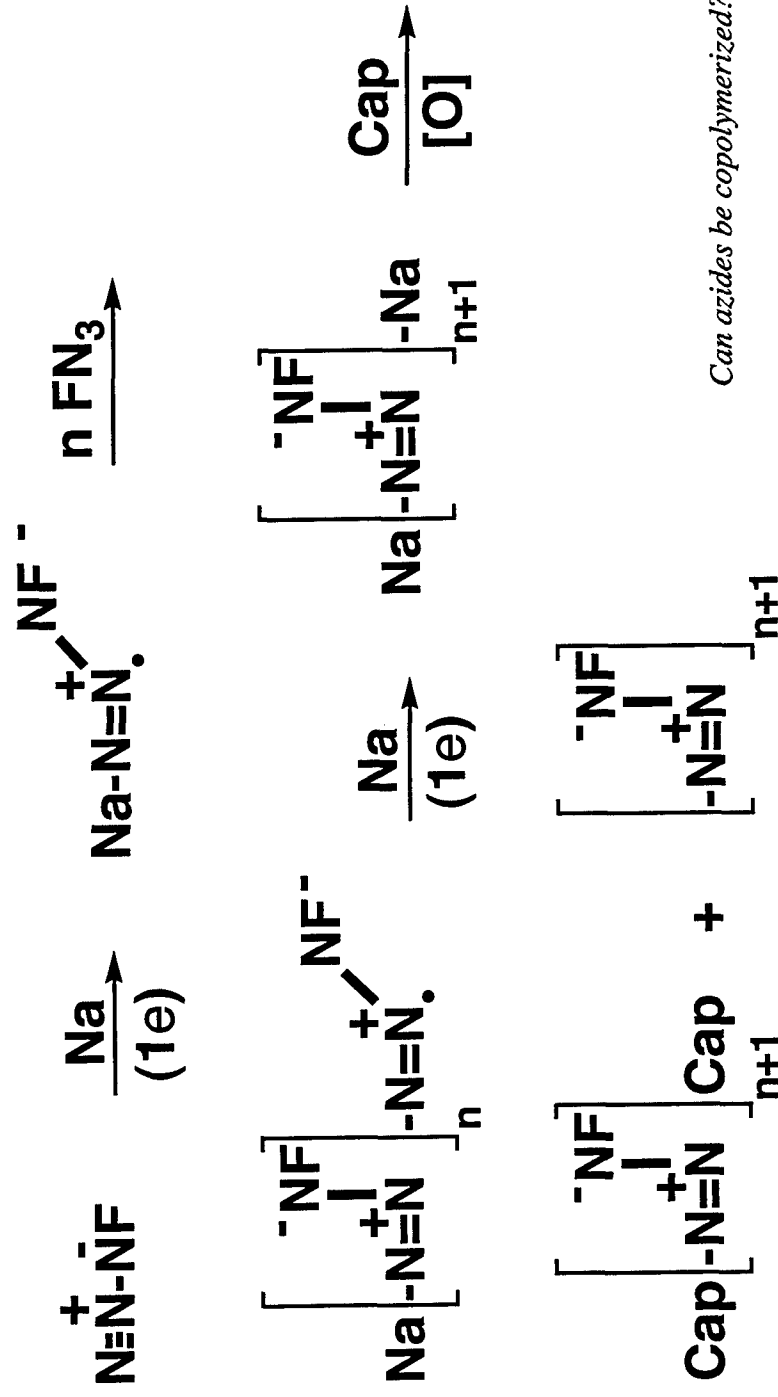
Polymerization of Nitrous Oxide



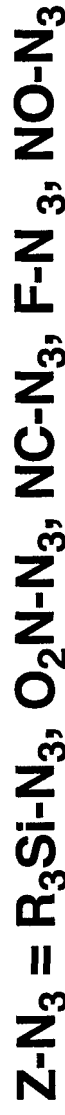
Can N_2O and/or azides be polymerized or copolymerized? Will N_2O undergo catalyzed cyclooligomerization or cyclopolymerization? Moscow thinks so. At OSU it is known that N_2O adds to acetylenes to give α -diazo carbonyl compounds: $\text{RC}(\text{N}_2)\text{-C}(=\text{O})\text{R}$! Can N_2O and acetylenes be copolymerized? Such products should be of enormous interest as energetic materials.

Polymerization of Azides

Research ideas! Can FN_3 be polymerized?



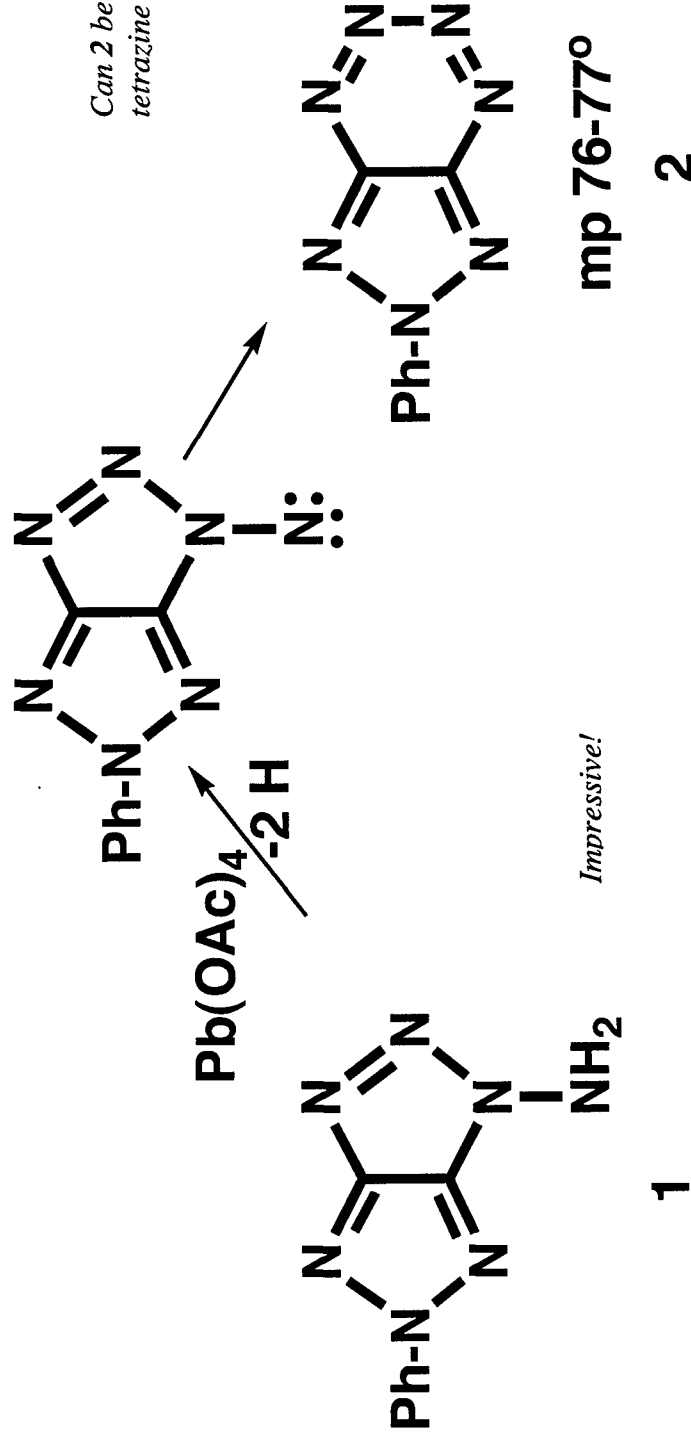
Can azides be copolymerized?



Active metals (Na, K, etc.) react with N_2O and azides! Can azides be polymerized and copolymerized? This will be of great significance if accomplishable. Will $\text{O}_2\text{N-N}_3$ add to double and/or triple bonds to give usable cycloadducts? Study of NC-N_3 should be sponsored.

Stable [1,2,3]-Triazolo[1,2,3,4]tetrazines

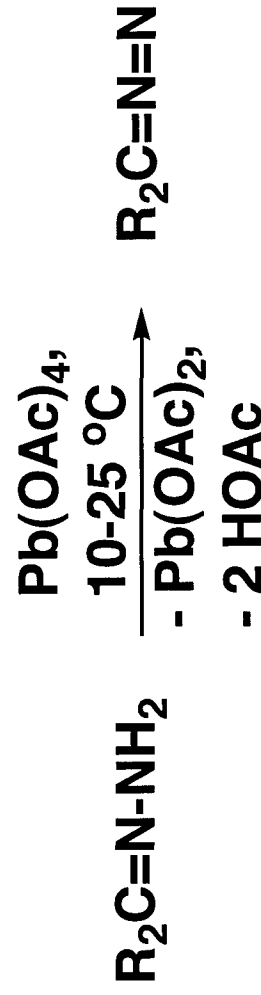
Aminoditriazole **1** is readily prepared. Analogs should be studied. Groups which are removable should be substituted for the phenyl substituent.



Ohsawa, Chem. Comm., 1988

Triazolotetrazine 2 is preparable and fairly stable. It is the only known 1,2,3,4-tetrazine and its chemistry should be determined. Tetrazine 2 cannot ring-open to a bis-diazo compound. Oxidation and derivatization of 2 should be studied. How important is the phenyl group in 2?

Oxidation of Hydrazones with $\text{Pb}(\text{OAc})_4$



Stabilizing groups are highly electronegative and conjugating: RO_2C , $\text{C}=\text{O}$, $\text{N}_2=\text{C}$, Ar , etc.



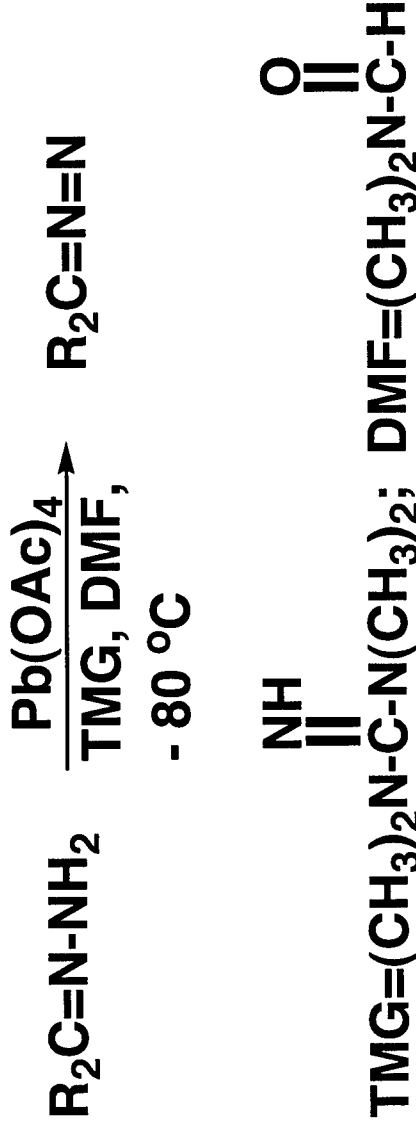
The acetic acid produced destroys the diazo compounds.

Holton (OSU); Venugopal (OSU-DARPA).

Monohydrazones are rapidly oxidized to monodiazocompounds by lead tetraacetate. Unless the diazo compounds are stabilized by conjugating groups, they are decomposed very rapidly by the acetic acid produced. This method is not usable for synthesis of typical diazo compounds. Of interest at OSU (Holton) was development of methodology in which the diazo compounds are not destroyed by acetic acid and elevated temperatures. Can *bis*-diazocompounds and/or 1,2,3,4-tetrazines be prepared by oxidation of *bis*-hydrazones? Can such methodologies be used in practical preparations of DTTO and/or IsoDTTO?

Oxidation of Hydrazones with $\text{Pb}(\text{OAc})_4$ in Tetramethylguanidine/Dimethylformamide

Can vicinal-dihydrazones be oxidized to usable bis-diazo compounds and/or 1,2,3,4-tetrazines?



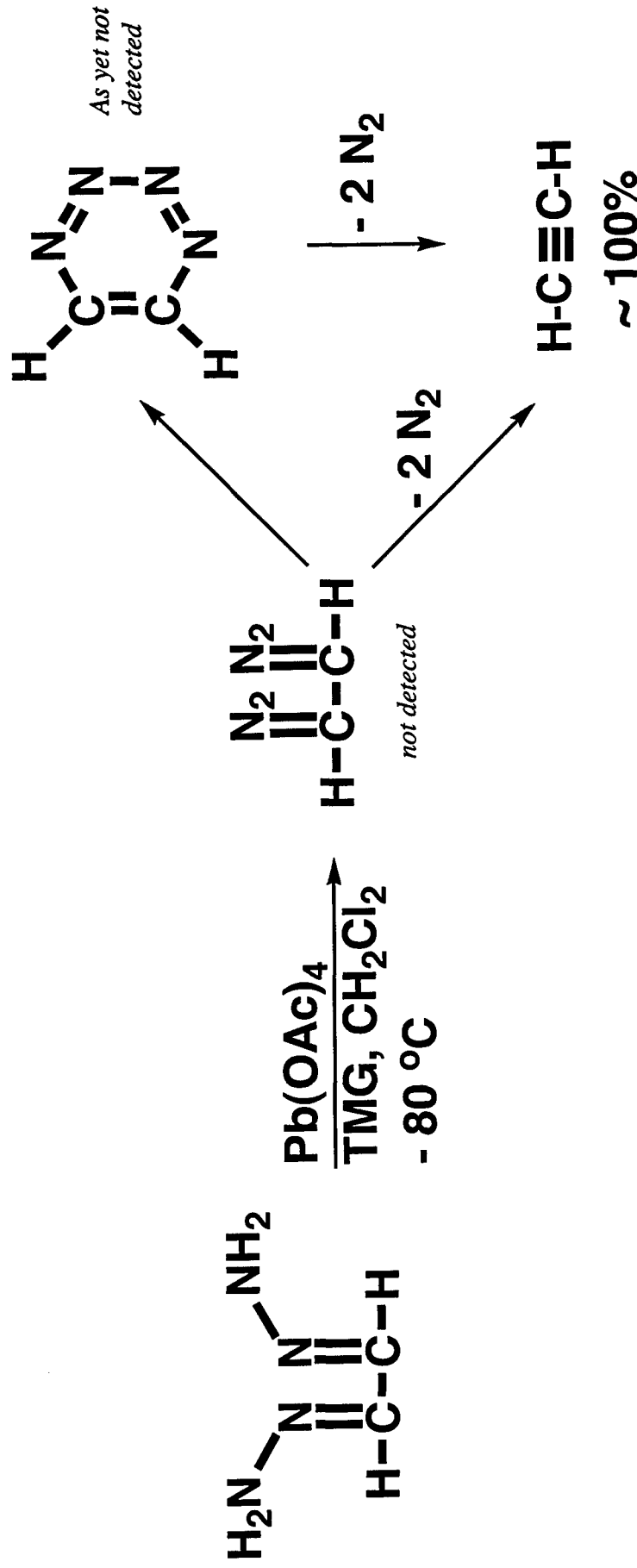
The TMG neutralizes the acetic acid and protects every mono-diazo compound as yet prepared. Is the method usable for practical syntheses of vicinal bis-diazo compounds or 1,2,3,4-tetrazines? The DMF serves as an excellent solvent for the above reaction mixtures at low temperatures. The mono-diazo compounds have been kept for days at $-78\text{ }^\circ\text{C}$ without decomposition.

**Excellent General Method;
Holton et al (OSU) *J. Org. Chem.*, 1995**

The above oxidation is the best known method for preparing monodiazo compounds at low temperatures. This method was originated at Ohio State and published as indicated. Of present interest as sponsored by DARPA/Air Force is extension of the method to vicinal-dihydrazones for practical syntheses of usable 1,2,3,4-tetrazines for energetics.

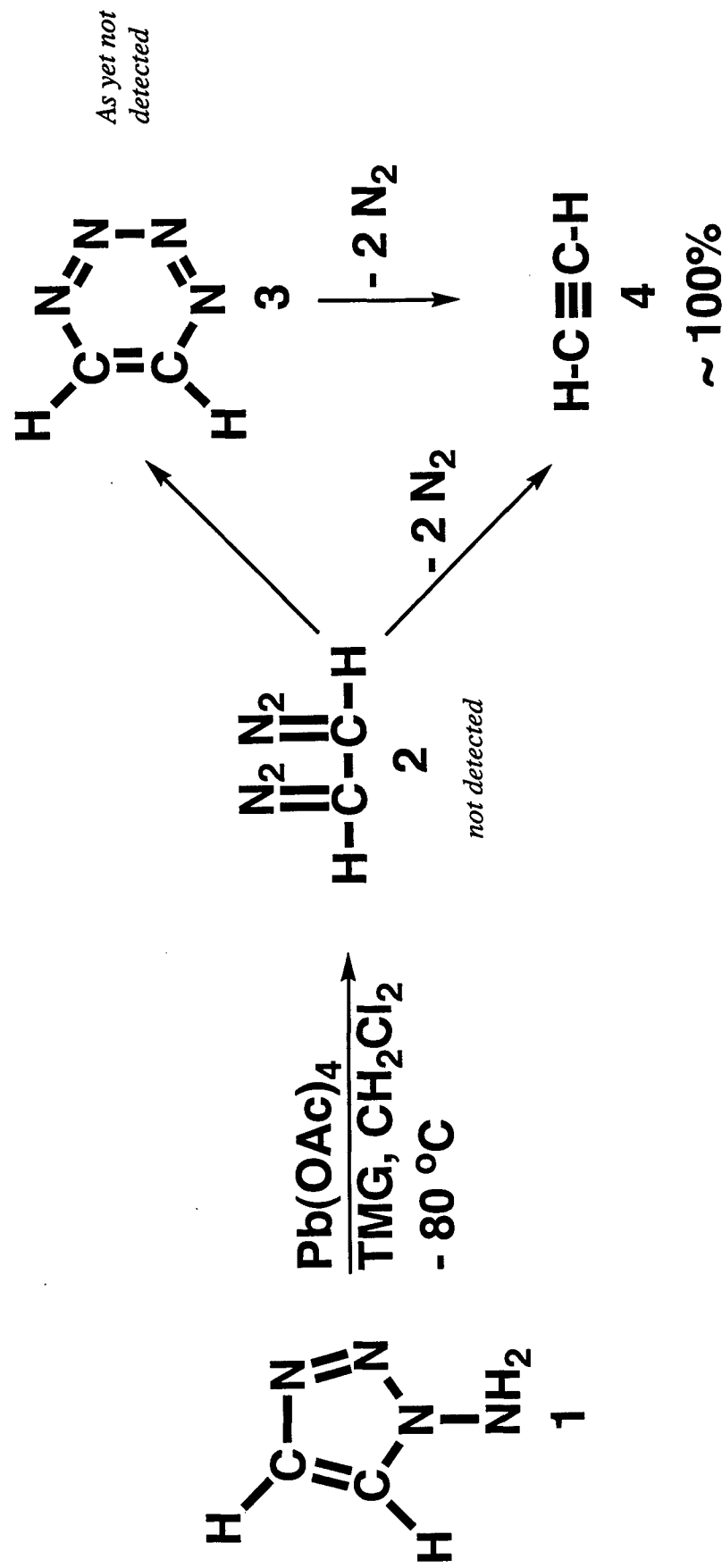
Glyoxal Dihydrazones, $\text{Pb}(\text{OAc})_4$, TMG, and CH_2Cl_2

Research by Dr. Venugopal (OSU-DARPA)



Reactions of glyoxal hydrazones with $\text{Pb}(\text{OAc})_4$ occur essentially instantly at temperatures as low as -120°C to give acetylene essentially quantitatively. It is not known if 1,2,3,4-tetrazine is actually produced in these experiments. At very low temperatures the reagents are not very soluble. The oxidations should be tried in liquid CO_2 at low temperatures. Is the bis-diazo intermediate formed? Spectroscopic studies should be made!

We want to study the oxidative properties of lead tetratriflate, $\text{Pb}(\text{O}_3\text{S}-\text{CF}_3)_4$!



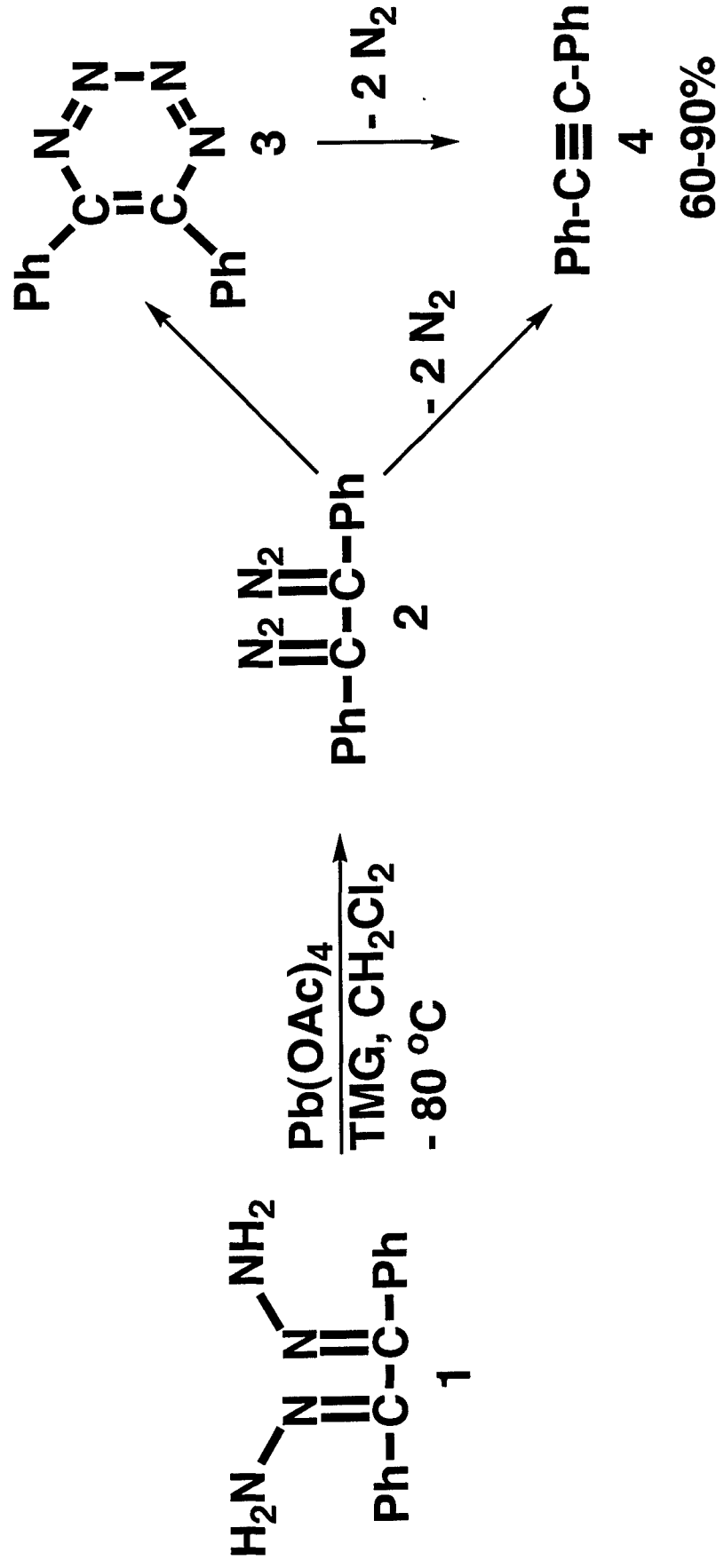
Of interest are the oxidative behaviors of 1-amino-1,2,3-triazoles and Pb(OAc)_4 in TMG at -80°C or even lower temperatures. What is the behavior of 1-nitro-1,2,3-triazole? What is found is that 1 oxidizes with loss of 2N_2 at $< -80^\circ\text{C}$. The behavior above is identical with that for glyoxal dihydrazones on page 18.

1,2,3,4-Tetrazine or 1,2-bis-diazoethane is unstable at -80°C and decomposes to acetylene (100%).

The system should be studied spectroscopically at low temperatures to detect intermediates and determine the reaction mechanism(s).

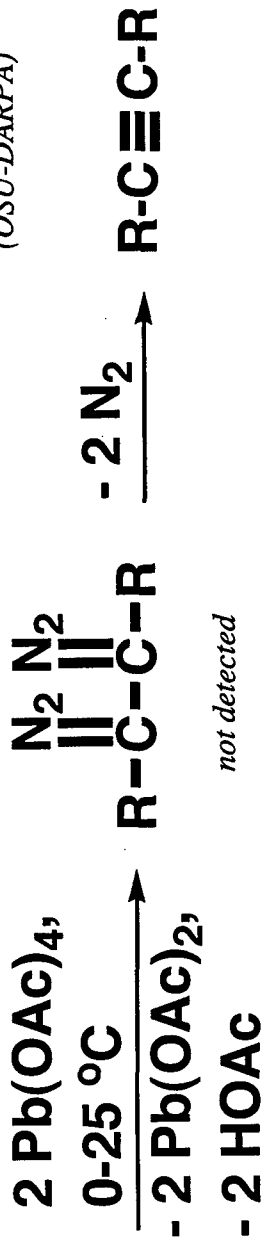
Benzil Dihydrazones, $\text{Pb}(\text{OAc})_4$, TMG, and CH_2Cl_2

Research by Dr. Venugopal (OSU-DARPA)

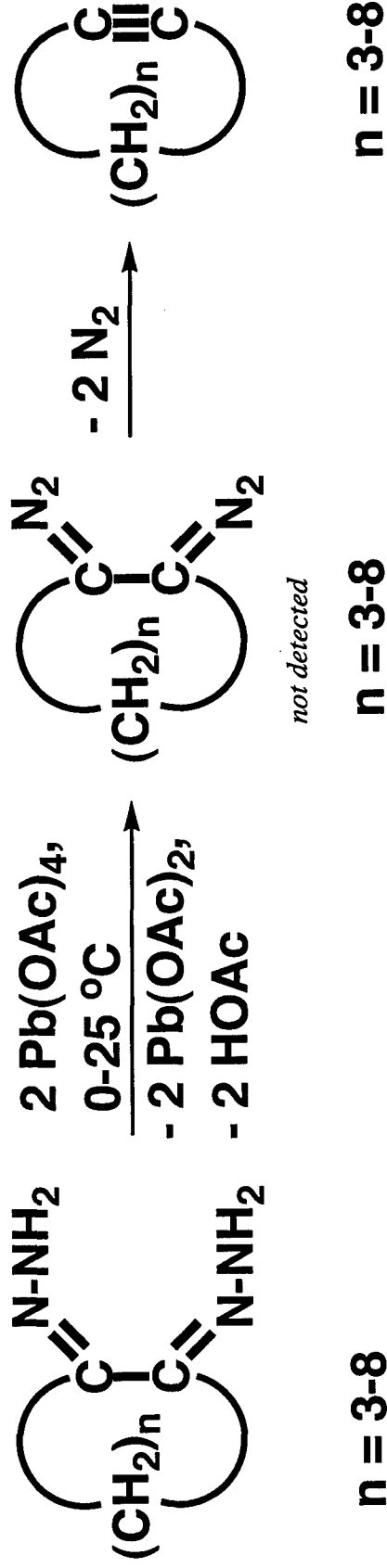


Benzil dihydrazones (1) have been found to be converted essentially instantly by lead tetraacetate at -80°C to diphenylacetylene (4). The solubilities of the reagents in all solvents tried are poor at temperatures of -120°C . It has thus not been possible to determine if 5,6-diphenyltetrazine (3) has life and can be oxidized to tetrazine oxide derivatives. Similar results have been obtained with biacetyl dihydrazones; 2-butyne is formed ($\sim 100\%$).

Oxidation of *Vic*-dihydrazones with $\text{Pb}(\text{OAc})_4$

$$\begin{array}{c} \text{NH}_2 \\ | \\ \text{N} \\ || \\ \text{N} \\ | \\ \text{H}_2\text{N} \end{array} \quad \begin{array}{c} \text{R} \\ | \\ \text{C} \\ || \\ \text{C} \\ | \\ \text{R} \end{array}$$


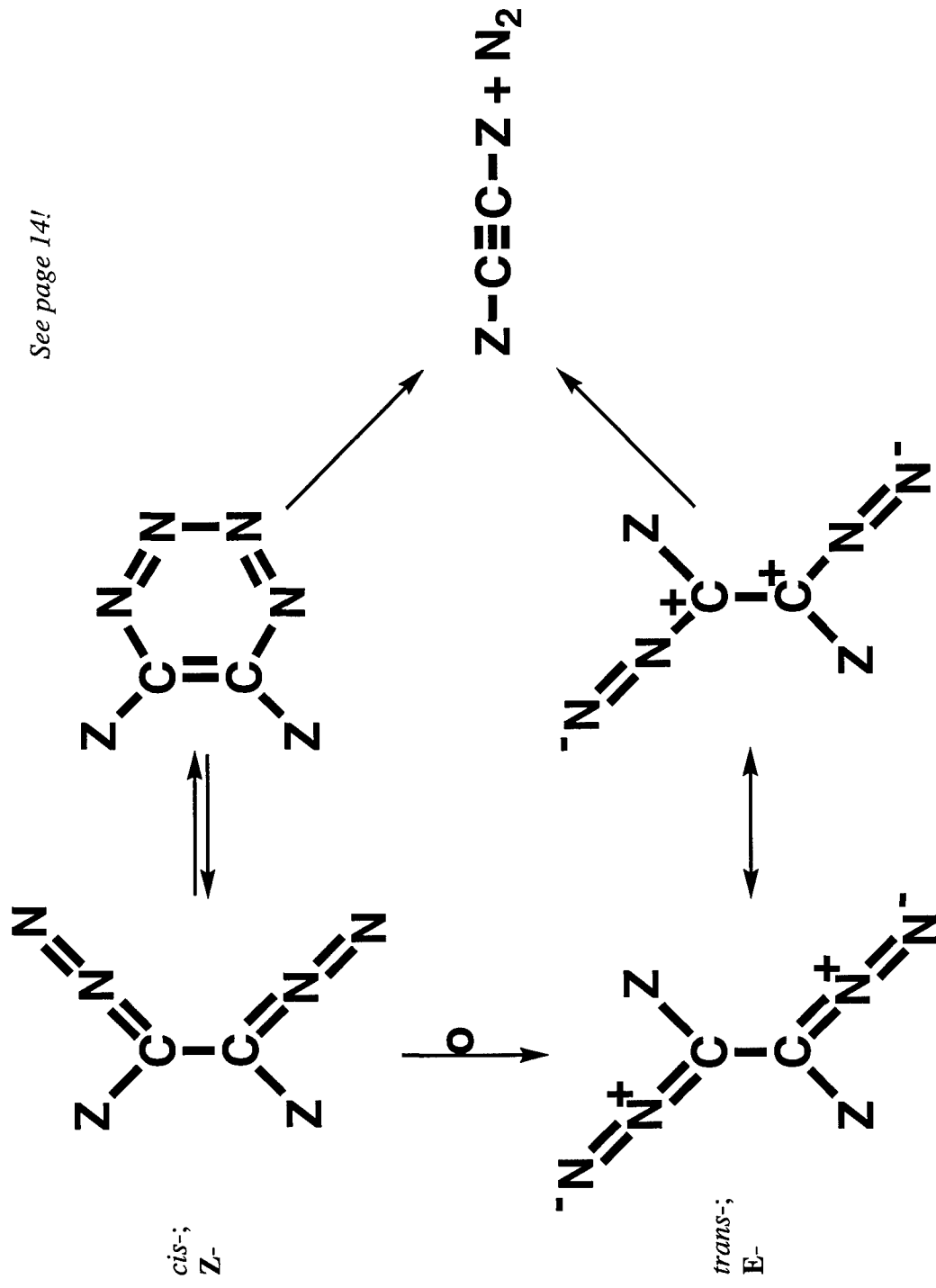
Research by Dr. Venugopal (OSU-DARPA)



This overhead summarizes the results of oxidizing open-chain and cyclic vicinal-dihydrazones with $\text{Pb}(\text{OAc})_4$, TMG , and CH_2Cl_2 . Acetylenes, even cyclopentyne, are produced in excellent yields. Of future interest is oxidation of 1,2-cyclobutanedione dihydrazones with $\text{Pb}(\text{OAc})_4$ to yield cyclobutynes, an enormously strained cyclic acetylene, and detectable reaction intermediates.

Vic-bis-diazo Compounds or 1,2,3,4-Tetrazines

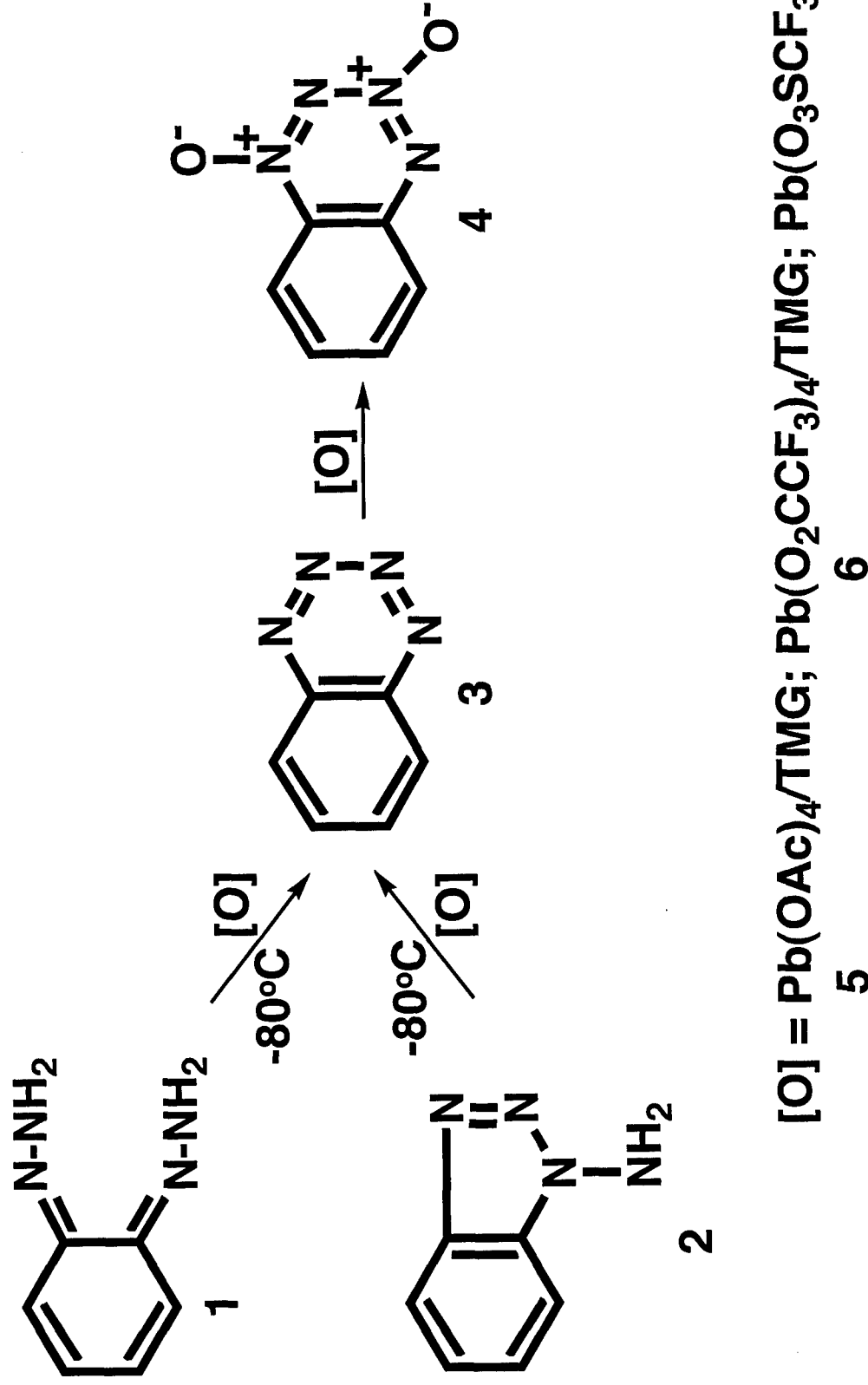
Research by Dr. Venugopal
(OSU-DARPA)



Why are bis-diazo compounds so unstable whereas *mono-diazo* compounds are not? Is stereochemistry very important? Are the two positive charges on adjacent carbon making bis-vicinal-diazo compounds so unstable? These important mechanism questions will be studied further.

Possible Synthesis of Tetrazine 1,3-Di-N-oxides

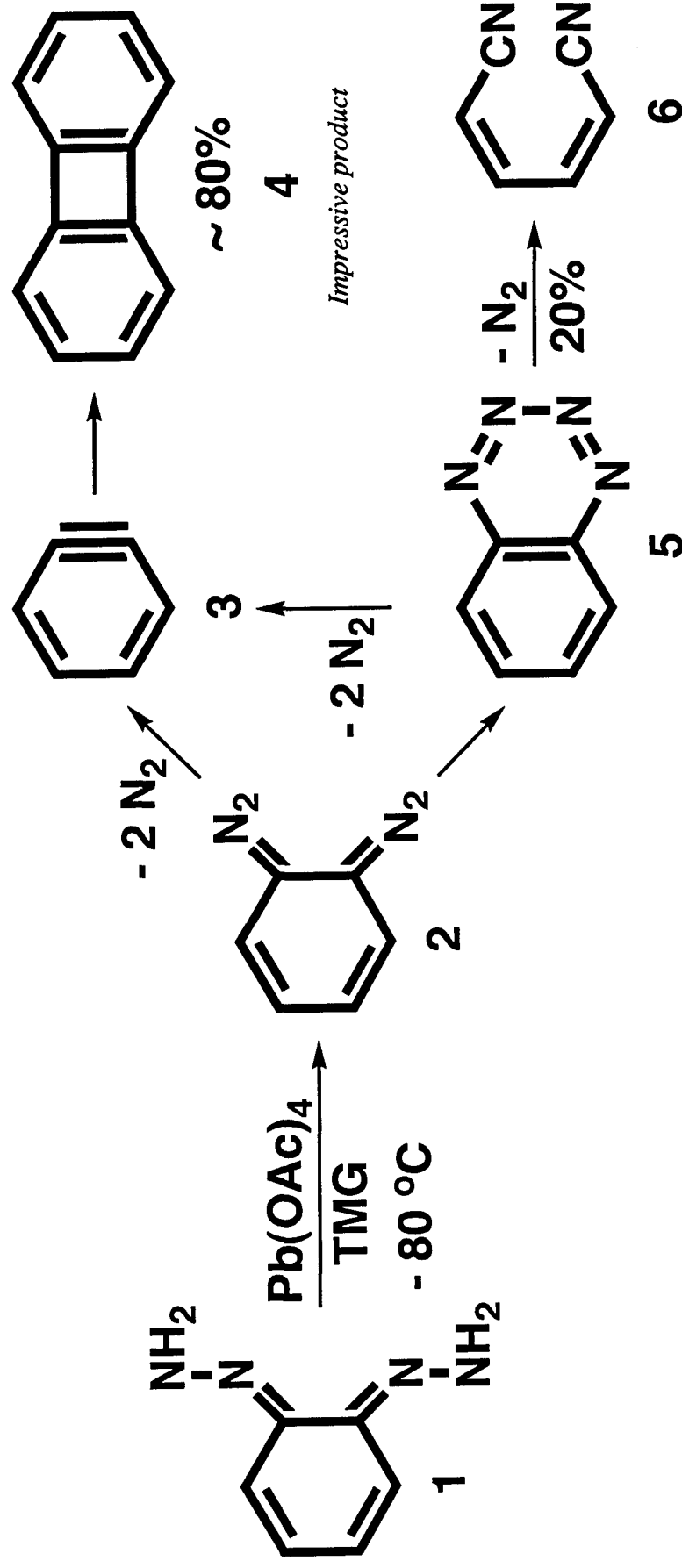
Research by Dr. Venugopal
(OSU-DARPA)



Study has been initiated of oxidative conversions of 1 and 2 to 3 as a possible practical source of 4. Oxidizing agent 6 is much more powerful than $\text{Pb}(\text{OAc})_4$ and can be used at lower temperatures than 5.

Oxidation of *o*-Quinone Dihydrazones with $\text{Pb}(\text{OAc})_4$

Research by Dr. Venugopal (OSU-DARPA)

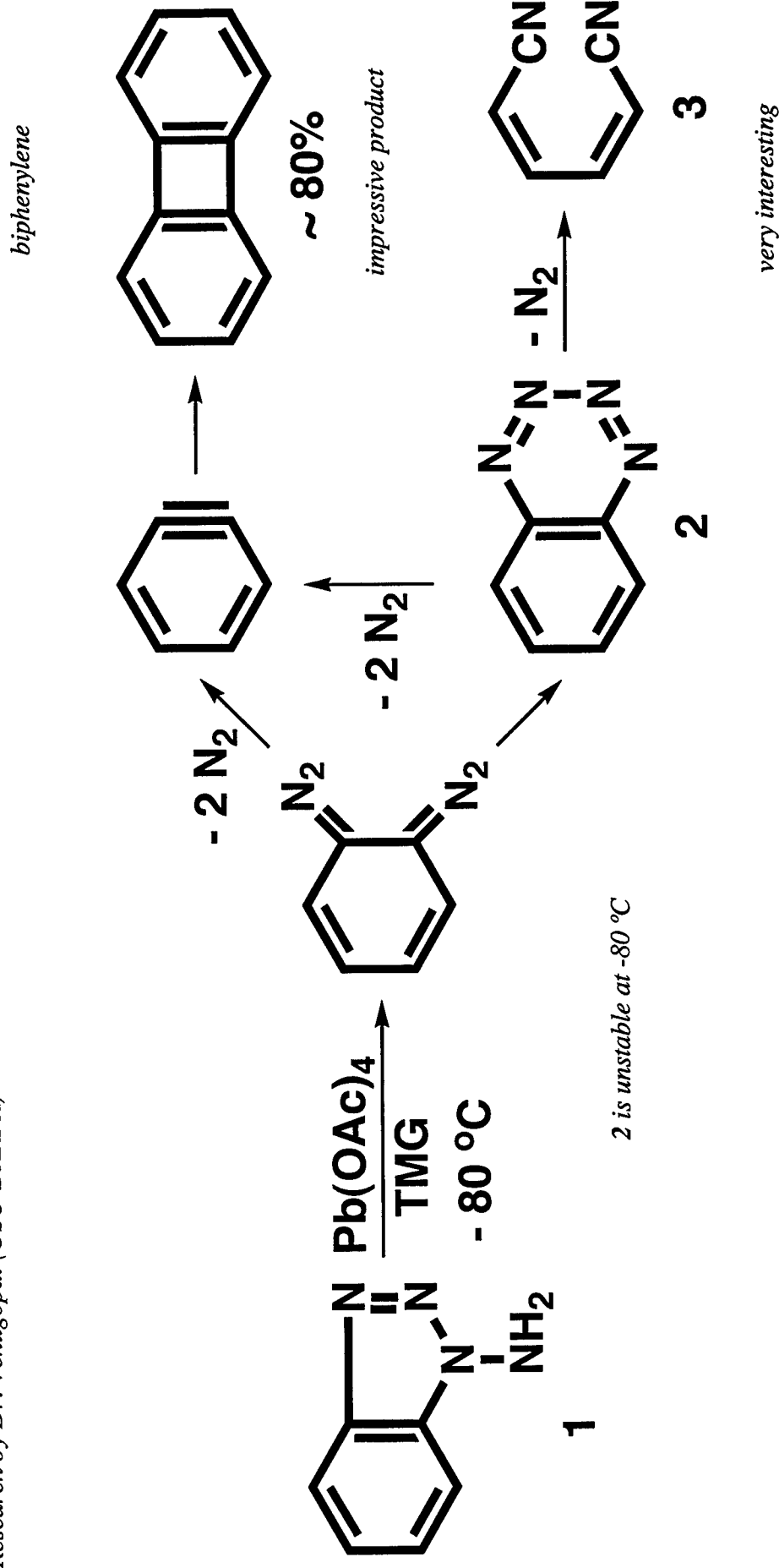


Investigation: Lower Temperatures; Solvents; IR; Oxidants; Traps

Oxidation of 1 by $\text{Pb}(\text{OAc})_4$ /TMG at temperatures as low as -100°C yields biphenylene ($\sim 80\%$) and 1,4-dicyano-1,3-butadiene ($\sim 20\%$). Benzotetrazine (5) could not be detected. Can the oxidations be effected at lower temperatures to give 2 and/or 5? What will happen with other oxidants?

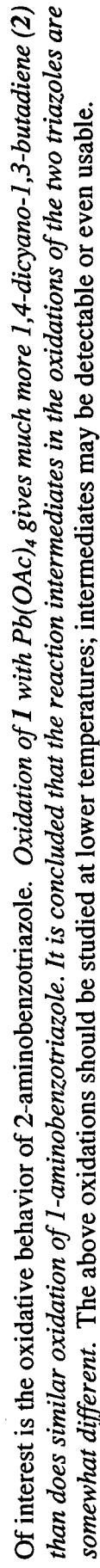
Oxidation of 1-Aminobenzotriazole

Research by Dr. Venugopal (OSU-DARPA)



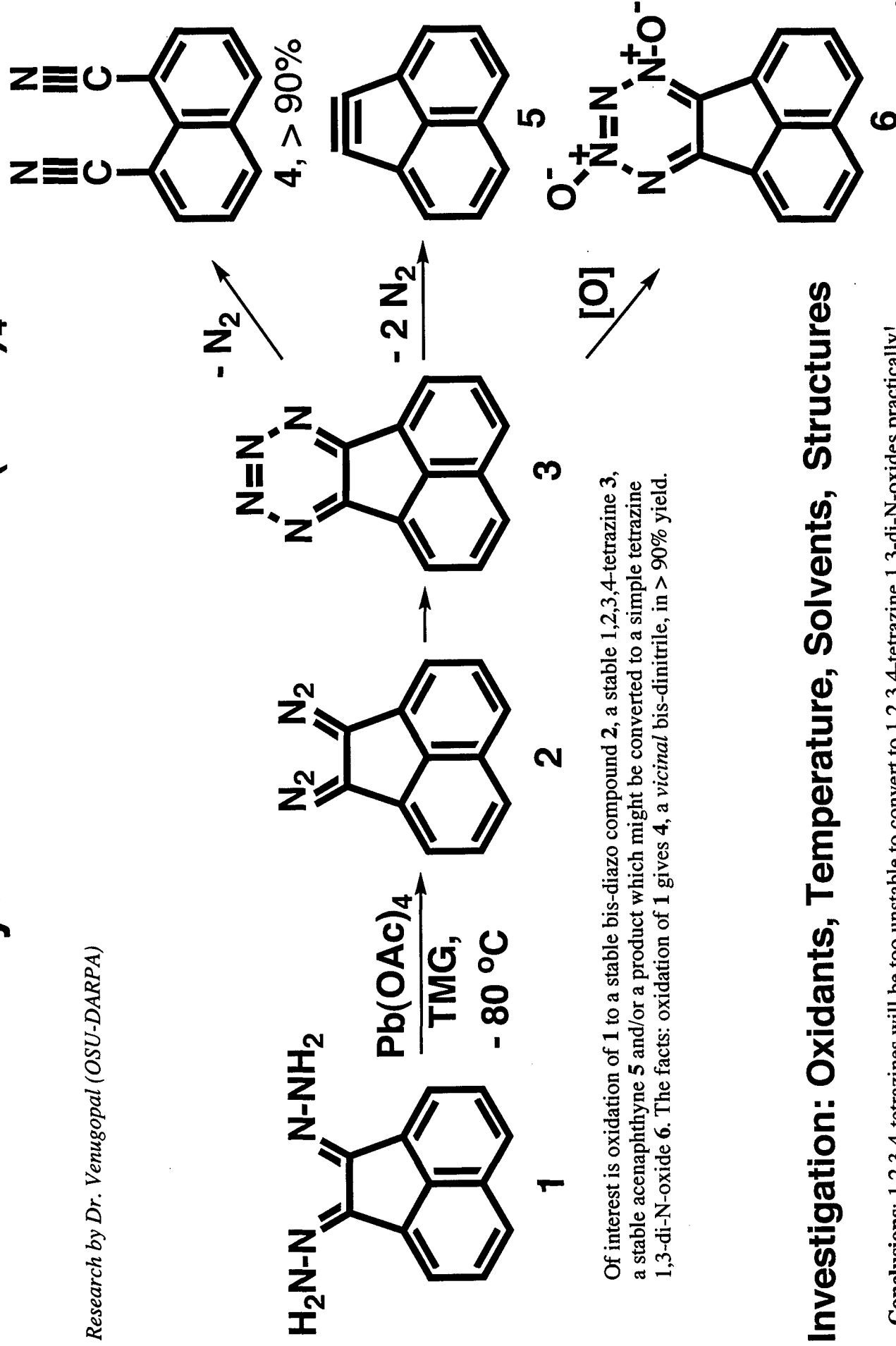
The oxidative behavior of 1-aminobenzotriazole is of interest. Will the products of reaction of 1 be the same as that of *o*-quinone dihydrazones (overhead 24)? The products of oxidation of 1 by Pb(OAc)_4 are found to be essentially identical with that from *o*-quinone dihydrazones. Tetrazine 2 has as yet not been detected. Of note is that 1,4-dicyano-1,3-butadiene (3) is a product of oxidation of 1 with Pb(OAc)_4 .

Research by Dr. Venugopal (OSU-DARPA)



Oxid'n of Acenaphthenequinone Dihydrazones with $\text{Pb}(\text{OAc})_4$

Research by Dr. Venugopal (OSU-DARPA)



Of interest is oxidation of 1 to a stable bis-diazo compound 2, a stable 1,2,3,4-tetrazine 3, a stable acenaphthine 5 and/or a product which might be converted to a simple tetrazine 1,3-di-N-oxide 6. The facts: oxidation of 1 gives 4, a vicinal bis-dinitrile, in $>90\%$ yield.

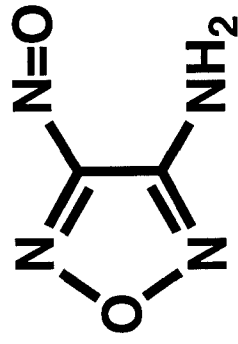
Investigation: Oxidants, Temperature, Solvents, Structures

Conclusions: 1,2,3,4-tetrazines will be too unstable to convert to 1,2,3,4-tetrazine 1,3-di-N-oxides practically!

FTDO (4) is being studied at OSU for possible practical synthesis of DITO.

Furazanotetrazine 4,6-Di-N-oxide (FTDO, 4)

FTDO (4) was first reported (Ioffe, Ph.D. Thesis, 1984, Moscow) and has been minimally described in a communication by Churakov et al (Zelinsky). We want to see this thesis! We cannot totally repeat the Russian work. Synthesis and study of reactions presently reported have received major attention at OSU from Dr. Venugopal.

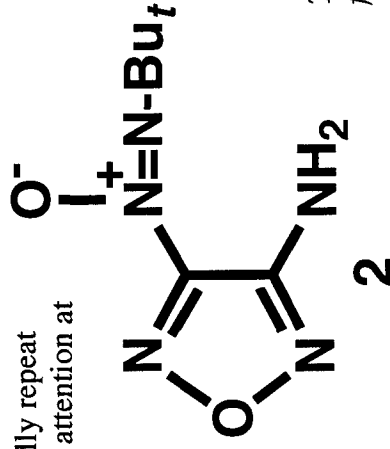


FTDO (4) is needed in large quantity. Synthesis of FTDO (4) has involved a major effort. This work should be continued.

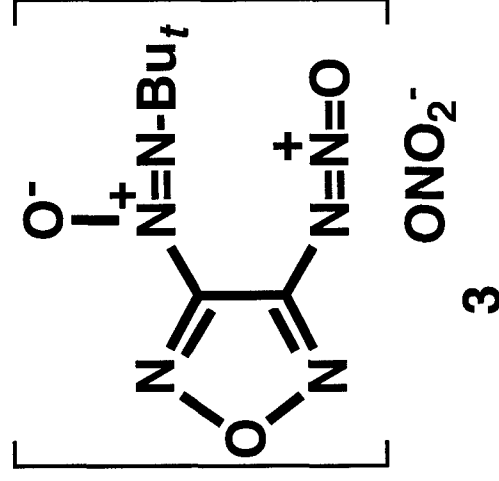
There are as yet no X-ray data reported for FTDO!



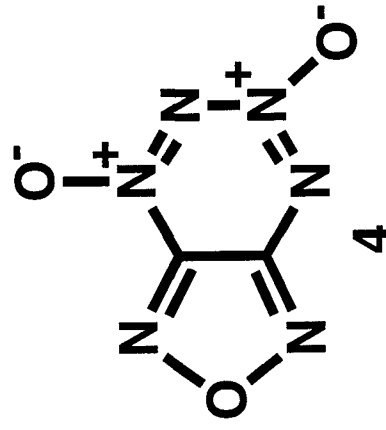
The mechanism of this reaction is not known!



The nitramine is first formed from 2 which then loses OH⁻ to give the R-N=N⁺=O intermediate (3) illustrated below.



Note the methodology and the mechanism of ring closure of 3. Product 4 does not give good crystals for X-ray work!



mp 110-113°

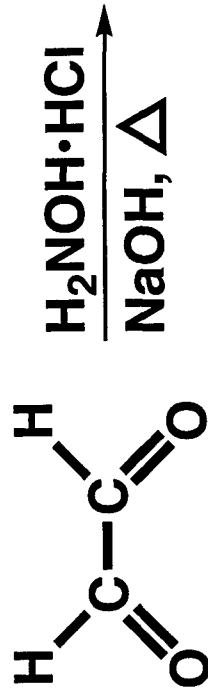
FTDO(4) was minimally described in a paper cited by Tartakovsky in his West Coast talk in 1995. No X-ray data are reported!

There are questions as to the structure of 4 cited below.

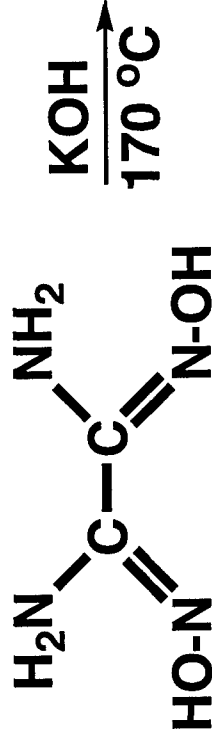
Churakov et al, Mendel. Commun., 1995, 227.

The Churakov method for preparing FTDO is based on that described much later for benzotetrazine 1,3-di-N-oxide.

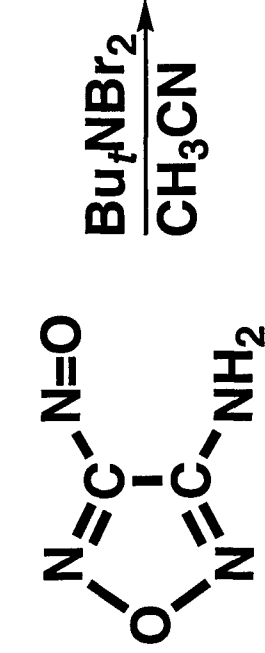
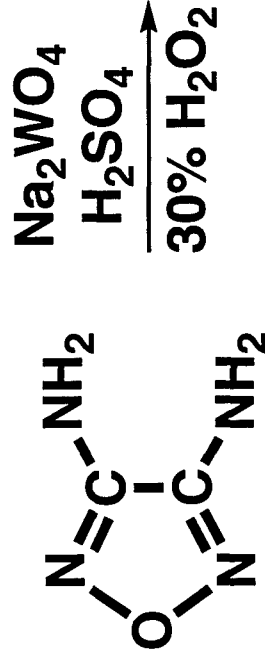
Furazanotetrazine 4,6-Di-N-oxide (FTDO, 2)



a commercial chemical.

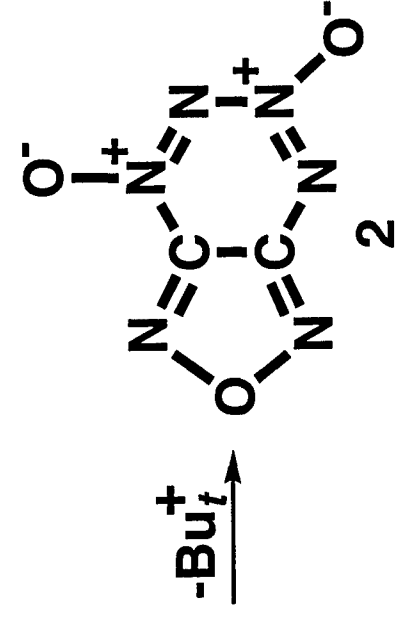
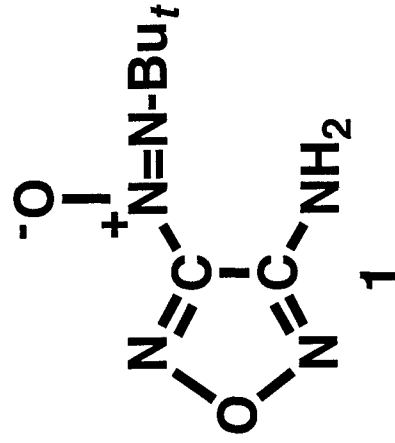


easily prepared, can be scaled up!



a diamine of great interest to the Air Force (Edwards)

work at OSU by Dr. Venugopal has resulted in improved synthesis of this nitrosoamine.

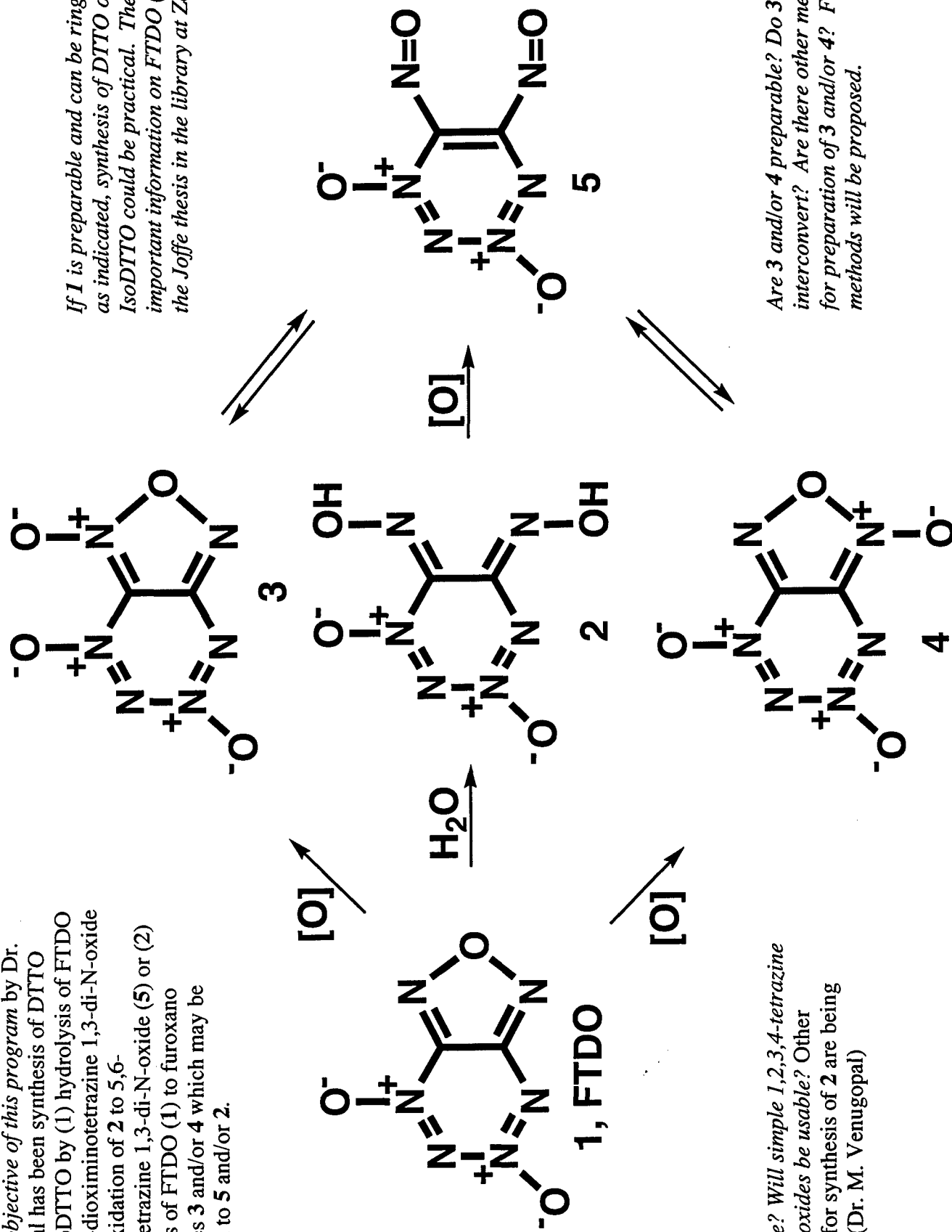


There are problems in converting 1 to 2! Because of limited funds these reactions have been run on small scale and are difficult to reproduce.

Nitronium triflate, $\text{O}_2\text{NOSO}_2\text{CF}_3$, has been found at OSU to be a better nitrating agent as above than NO_2BF_4 !

X-ray analysis of 2 has not been successful. The crystals have not been satisfactory! Is the structure correct?

A major objective of this program by Dr. Venugopal has been synthesis of DTTO and/or IsoDTTO by (1) hydrolysis of FTDO (1) to 5,6-dioximinotetrazine 1,3-di-N-oxide (2) and oxidation of 2 to 5,6-dinitrosotetrazine 1,3-di-N-oxide (5) or (2) oxidations of FTDO (1) to furoxano derivatives 3 and/or 4 which may be converted to 5 and/or 2.



If 1 is preparable and can be ring-opened as indicated, synthesis of DTTO or/and IsoDTTO could be practical. There is important information on FTDO (1) in the Joffe thesis in the library at Zelinsky!

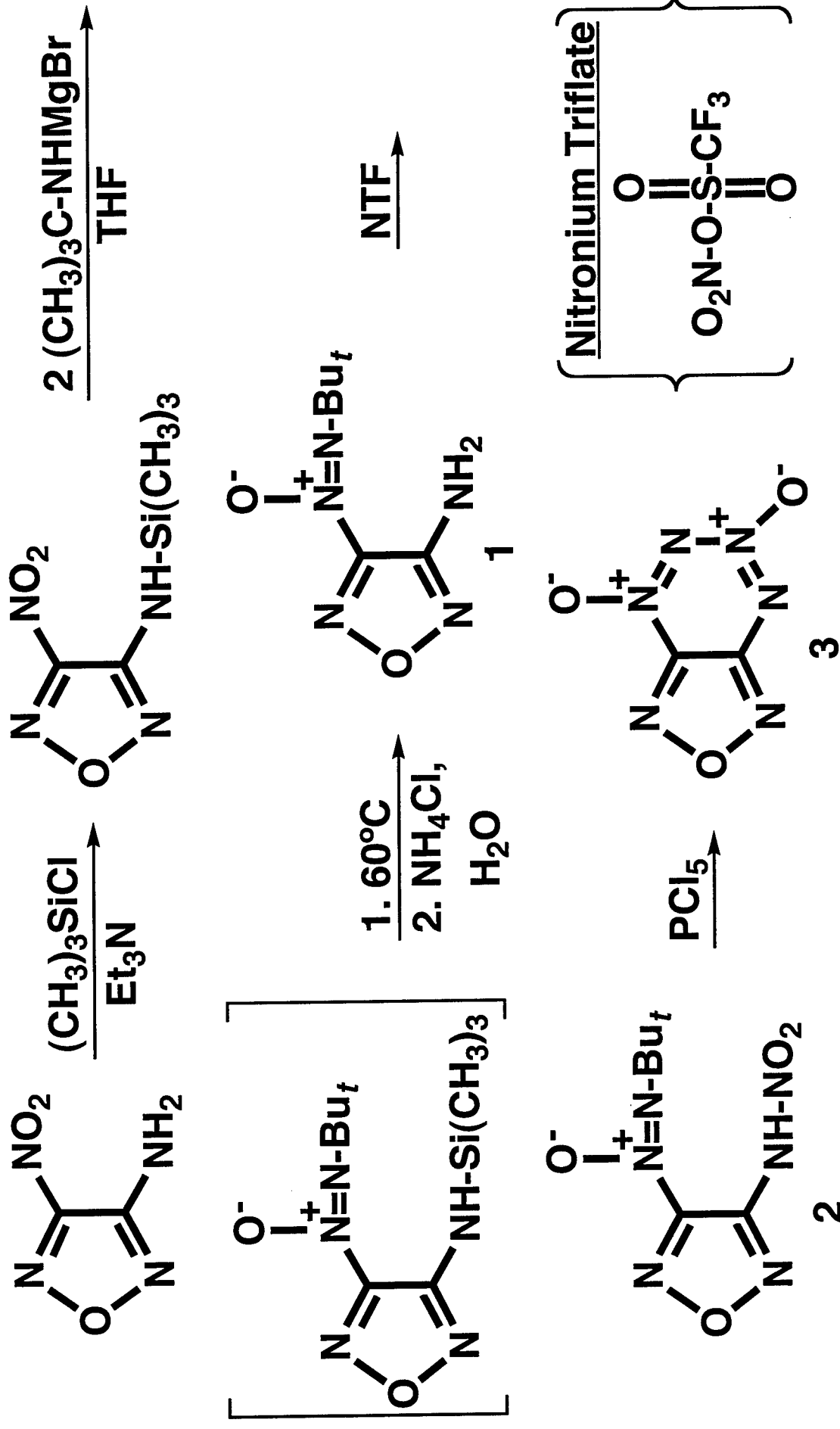
Is 2 stable? Will simple 1,2,3,4-tetrazine 1,3-di-N-oxides be usable? Other methods for synthesis of 2 are being studied. (Dr. M. Venugopal)

Are 3 and/or 4 preparable? Do 3 and 4 interconvert? Are there other methods for preparation of 3 and/or 4? Further methods will be proposed.

It is essential that FTDO (1) can be prepared efficiently. Moscow has a 10-15 year head start on this project. The Russians might publish their results before studies at OSU are completed. We need to know where Moscow is on synthesis and use of FTDO (1). The present study at OSU should be discussed further with its sponsors.

Dr. Venugopal (OSU-DARPA) has developed an important alternate synthesis of 1-amino-2-*t*-butylazoxyfuranan (1) for possible use in preparing FTDO (3).

Furazanotetrazine 1,3-Di-N-oxide (FTDO)

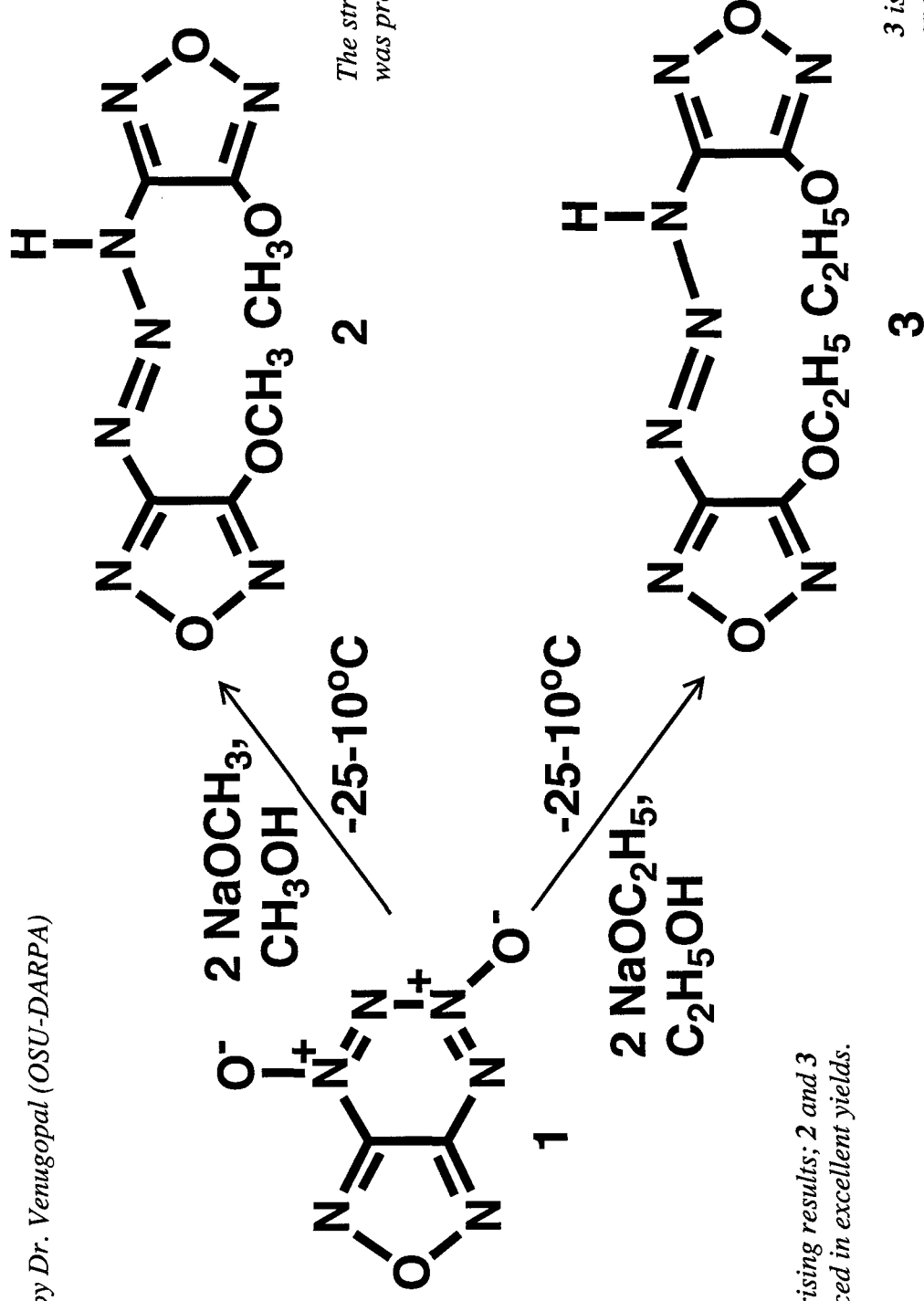


Venugopal (OSU-DARPA).

At present efforts at OSU to convert 1 to 3 have been unconvincing! Large quantities of 1 should be prepared! The chemistry of 1 should be studied in detail. Is the Russian structural assignment correct?

Reactions of Alkoxides with FTDO (1)

Research by Dr. Venugopal (OSU-DARPA)

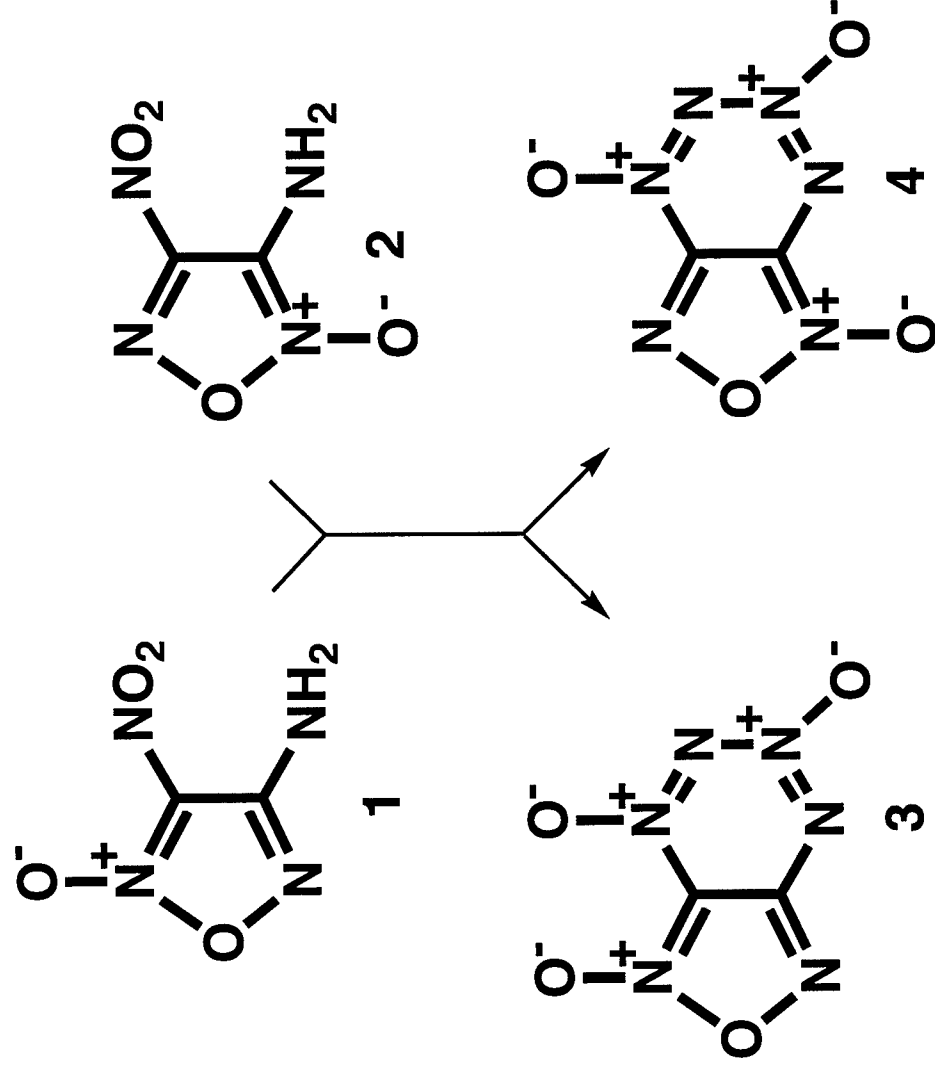


Very surprising results; 2 and 3 are produced in excellent yields.

FTDO (1) as presently prepared at OSU appears identical with that reported by Moscow. Hydrolysis of 1 yields complex products. Reactions of 1 with alkoxides give products (2 and 3) which are difficult to explain. Further study of the structure and behavior of 1 is necessary.

Synthesis of Furoxanotetrazine 1,3-Di-N-oxides

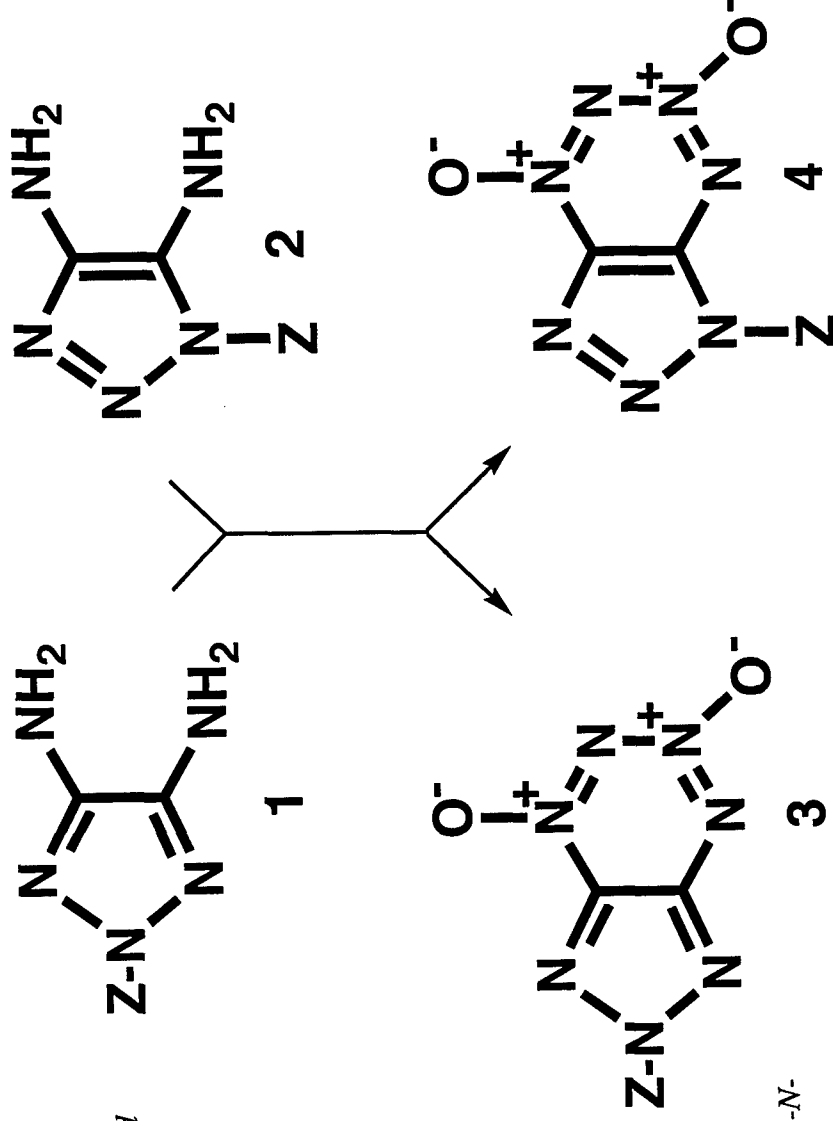
Very important future studies!



Aminonitrofuroxans 1 and 2 are known (Zelinsky). Use of Dr. Venugopal's methodologies may lead to effective syntheses of 3 and/or 4 which then may be used for preparations of DTTO and/or IsoDTTO. Furoxans 3 and 4 are isomers of DTTO and IsoDTTO.

Synthesis of Triazolotetrazine 1,3-Di-N-oxides

Moscow has synthesized and developed the chemistry of 4,5-diaminotriazoles 1 and/or 2.

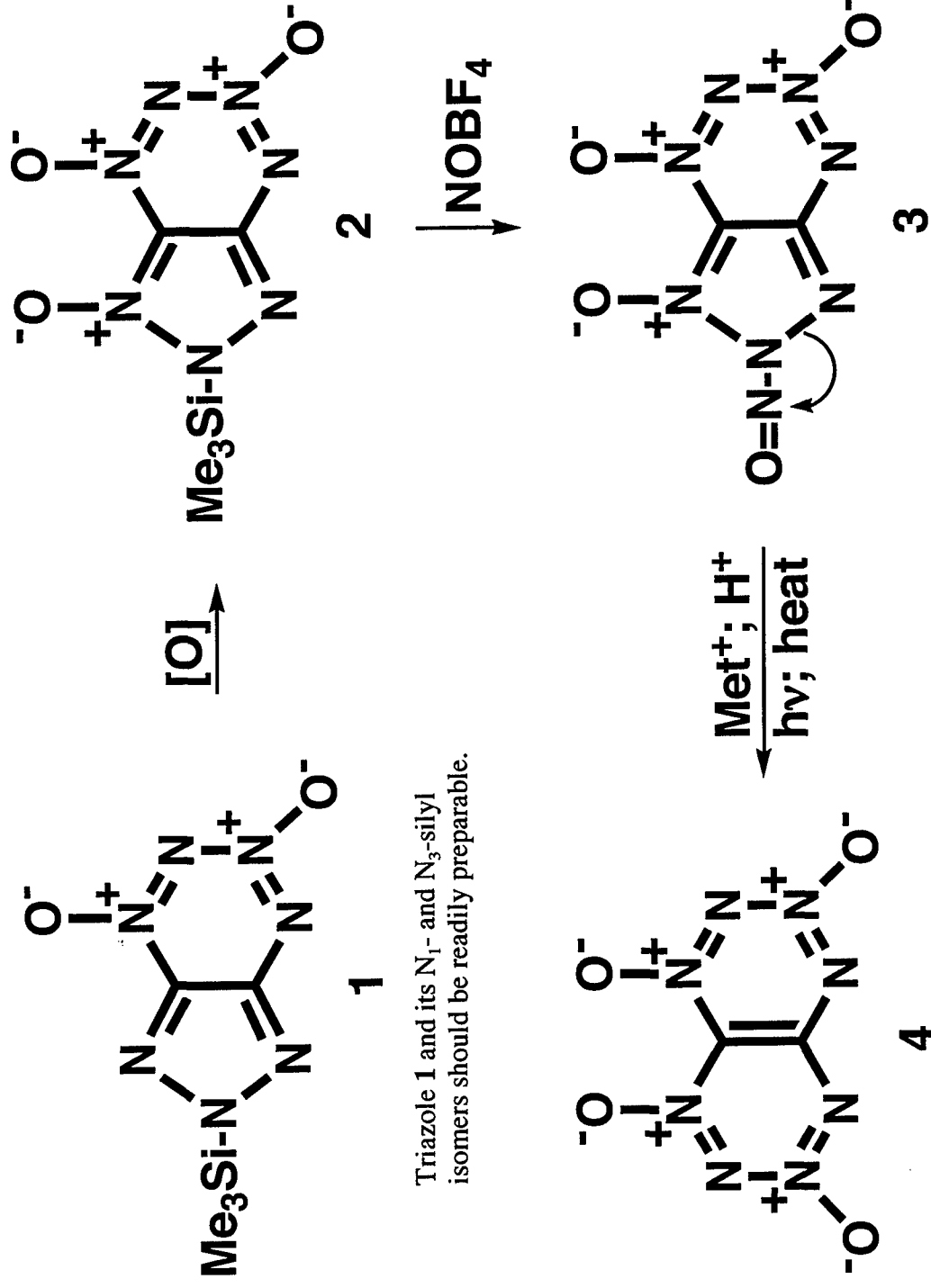


Can triazolotetrazine 1,3-di-N-oxides 3 and/or 4 be controllably prepared and hydrolyzed and then lead to DTTO and/or IsoDTTO?



Syntheses of diaminotriazoles 1 and 2 were to be initiated at OSU by Dr. D. Srinivasulu. These efforts were also to be parts of studies of syntheses of nitroacetylenes and dinitroacetylene. Triazolotetrazine 1,3-di-N-oxides 3 and/or 4 as prepared from 1 and/or 2 are also of interest in syntheses of DTTO and IsoDTTO.

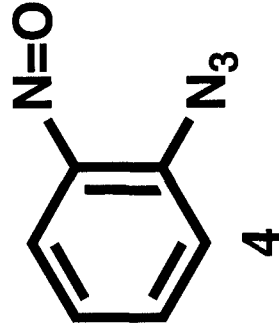
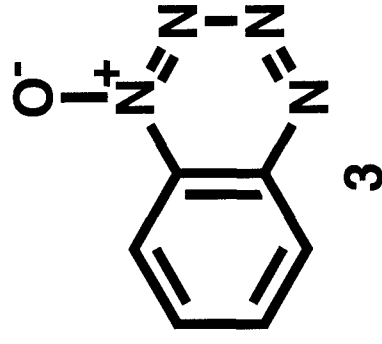
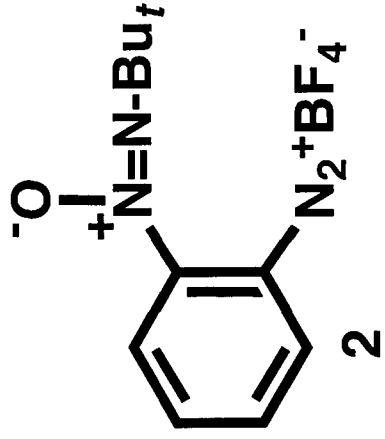
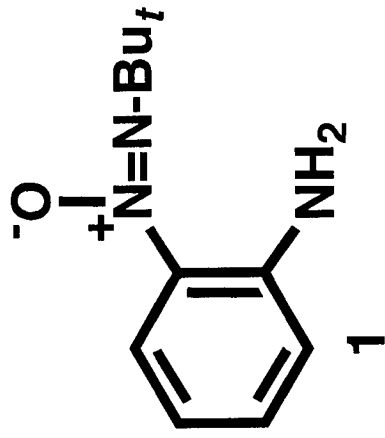
Possible Synthesis of DTTO



Triazole 1 and its N₁- and N₃-silyl isomers should be readily preparable.

The above sequence is an example of a possible synthesis of DTTO (4) from a triazolotetrazine di-N-oxide such as 1. Such an effort will be discussed in detail later. Hydrolyses of triazolotetrazine di-N-oxides are important synthesis and mechanistic research problems. Many other possible routes to DTTO and/or IsoDTTO will be proposed. Will DTTO and IsoDTTO be stable?

Synthesis of Benzotetrazine 1-N-oxide



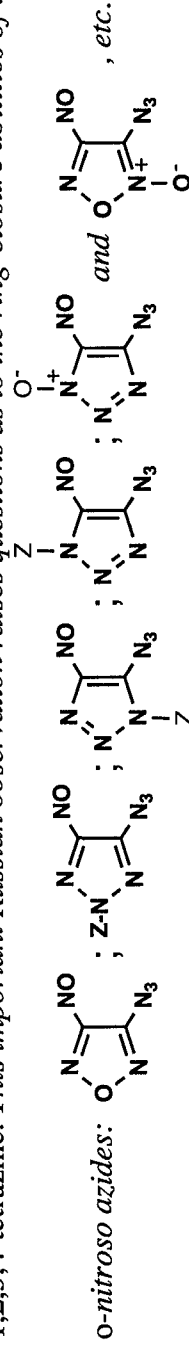
Little is known about *o*-nitroso azides and their ring-closure isomers! What are the behaviors of *cis*- and *trans*-azido(nitroso) olefins?

Very important Russian molecules!
Heating 1 yields benzotriazole and *t*-BuOH (Dr. Venugopal, OSU-DARPA).

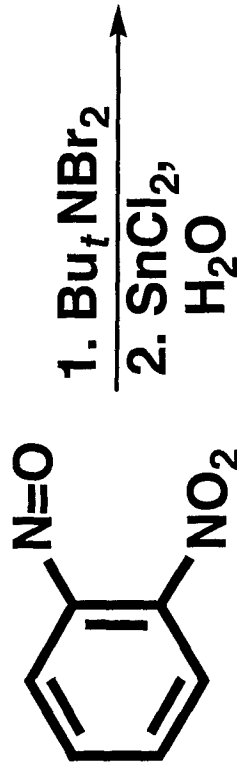
A stable product!
Can 3 be oxidized to benzotetrazine 1,3-di-N-oxide?
Do azides add to nitroso compounds?

An impressive new cyclization reaction by Zelinsky researchers.

2-Nitrosophenyl azide (4), prepared as above from *o*-(*t*-butylazoxy)aniline (1), ring closes to benzotetrazine 1-N-oxide (3), a fairly stable 1,2,3,4-tetrazine. This important Russian observation raises questions as to the ring-closure abilities of the following 5-membered ring

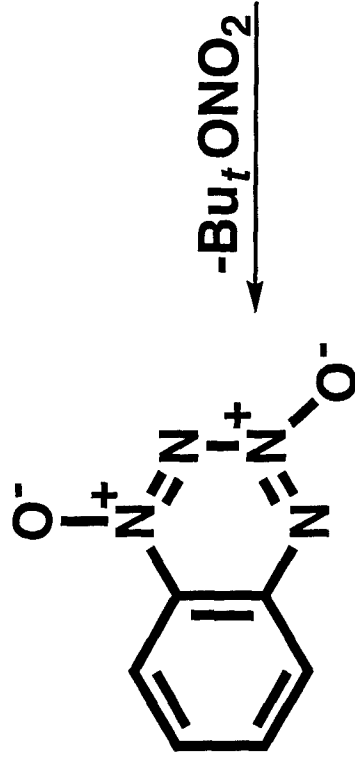


Synthesis of Benzotetrazine 1,3-Di-N-oxide

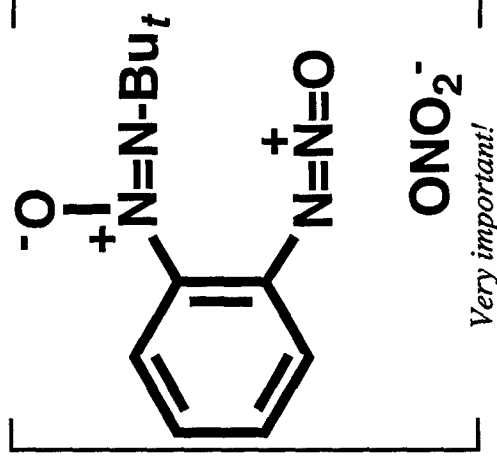
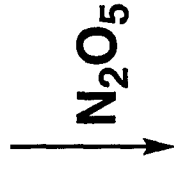
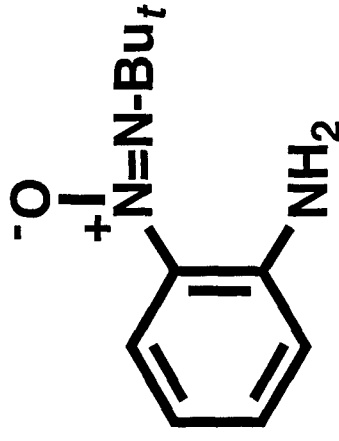


We now know that azides react with aromatic nitroso compounds with nitrogen loss to give azoxy compounds! Such syntheses of azoxy compounds should be developed further!

The present synthesis sequence is a major contribution that will have a great effect on future high-nitrogen chemistry.



*mp 177-179 °C
very stable!
biologically active!*



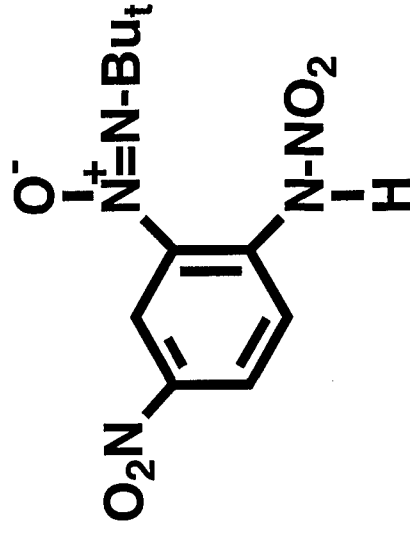
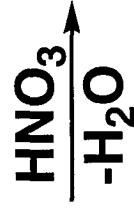
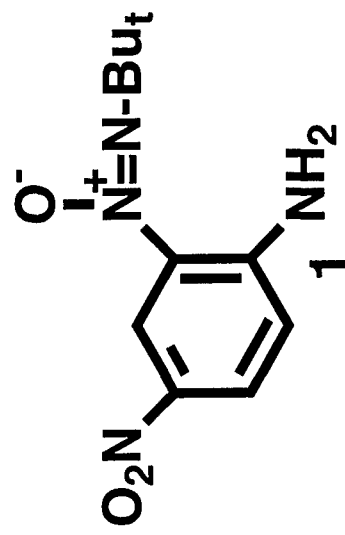
Very important!

A nitramine is first formed. We have greatly improved this Russian synthesis.

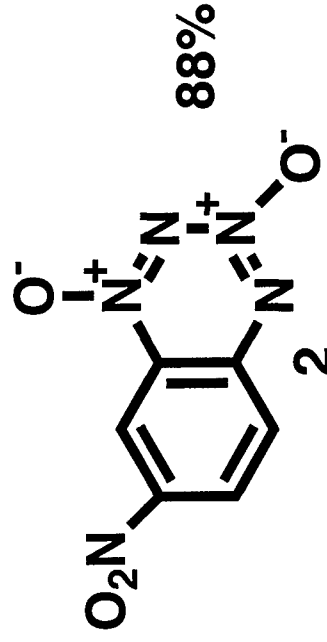
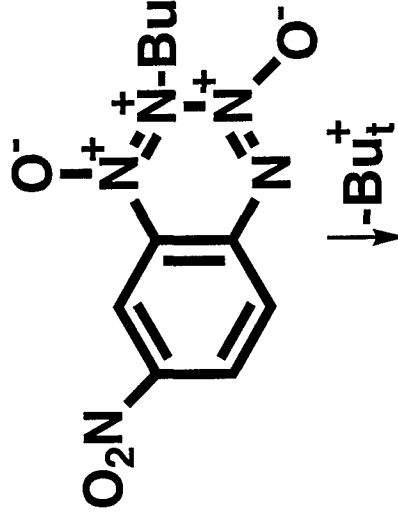
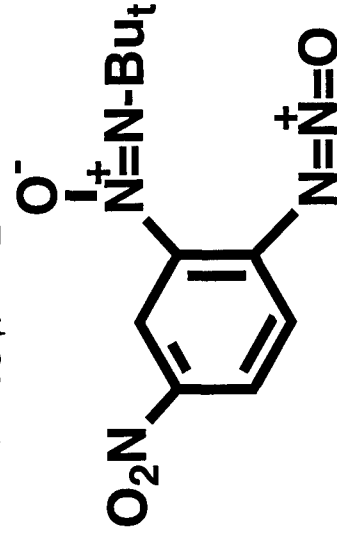
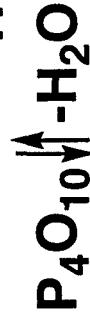
Generation of R-N=N=O intermediates is highly significant! R-N=N=N-R structures have now been generated at OSU!

Churakov, Mendel. Comm. 1991

This is an outstanding synthesis that has been ignored by U.S. pharmaceutical companies. They do not know of the reactions of 1,2,3,4-tetrazine 1,3-di-N-oxides that give nitric oxide and other nitrogen-oxygen products.



The P_4O_{10} reacts directly with the primary nitramine.



2 is a very stable compound.

An excellent overall synthesis; 5,7-dinitrobenzotetrazine 1,3-di-N-oxide has also been prepared in Moscow. Are such products valuable energetics?

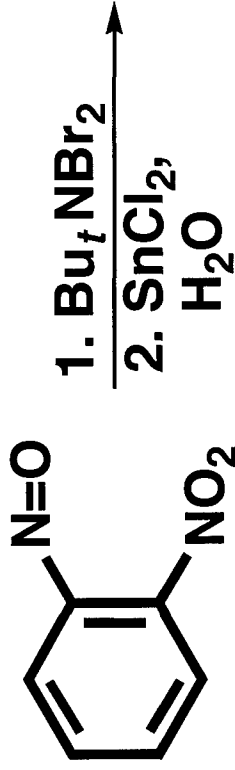
Another impressive ring-closure!

Frumkin et al, *Russ. Chem. Bull.* 2000, 49, 482

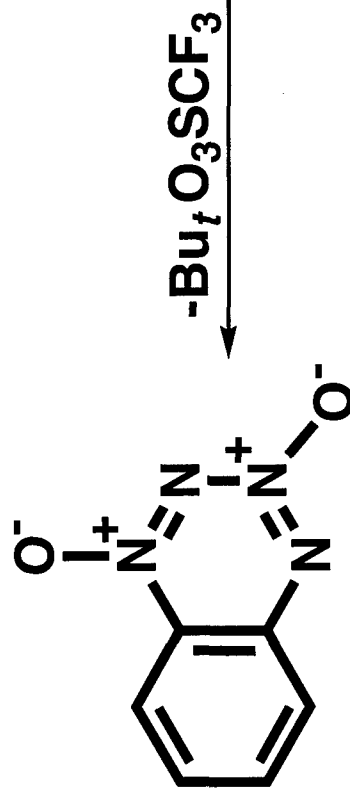
The Frumkin publication extends and improves the previous methodologies for preparing benzotetrazine 1,3-di-N-oxides. The nitro group in 2 is displaced readily by nucleophiles: OR^- , SR^- , CN^- , etc.

Synthesis of Benzotetrazine 1,3-Di-N-oxide

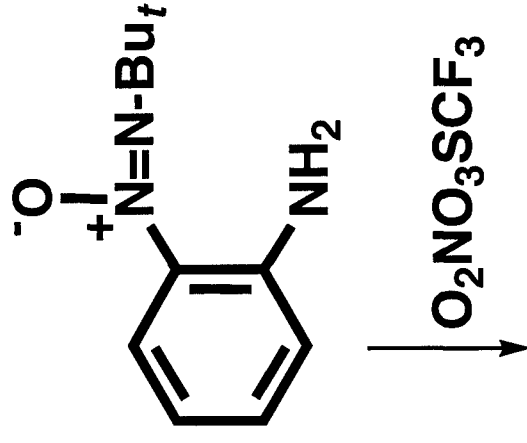
An improved synthesis at OSU using nitronium triflate, $O_2NO_3SCF_3$.



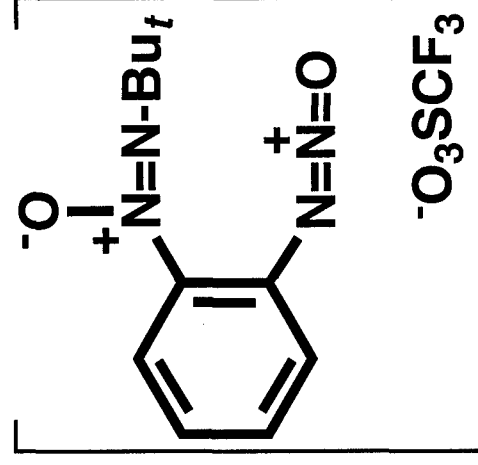
Study should be made of preparation of $O_2NO_3SCF_3$ from metal nitrates and CF_3SO_2Cl , a much cheaper method.



Nitronium triflate is generated in situ from $(CH_3)_4N^+NO_3^-$ and $(CF_3SO_2)_2O$, the Shackelford reagent!



Further uses of nitronium triflate for preparing nitramines are to be investigated at OSU.

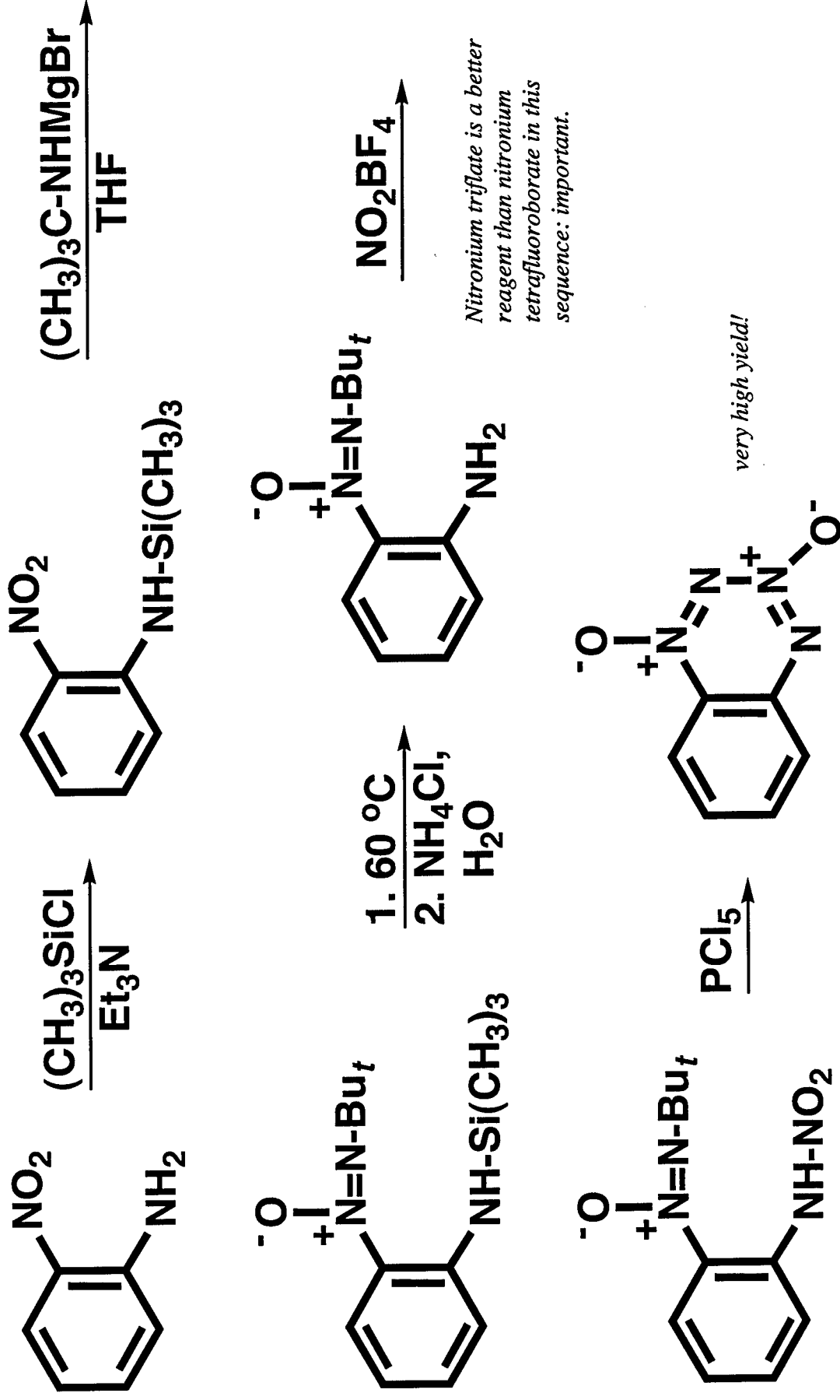


The nitrosative abilities of nitronium triflate should also be studied. Very important.

Venugopal (OSU-DARPA).

Benzotetrazine 1,3-Di-N-oxide

A new method for preparing benzotetrazine 1,3-di-N-oxide (OSU).

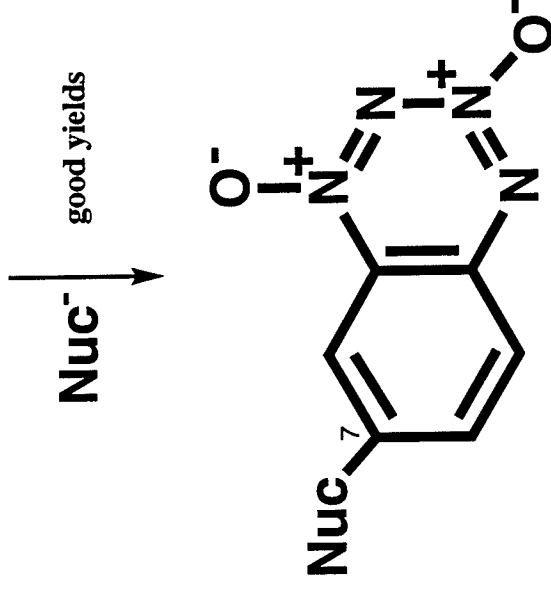
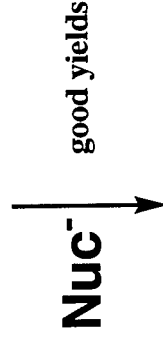
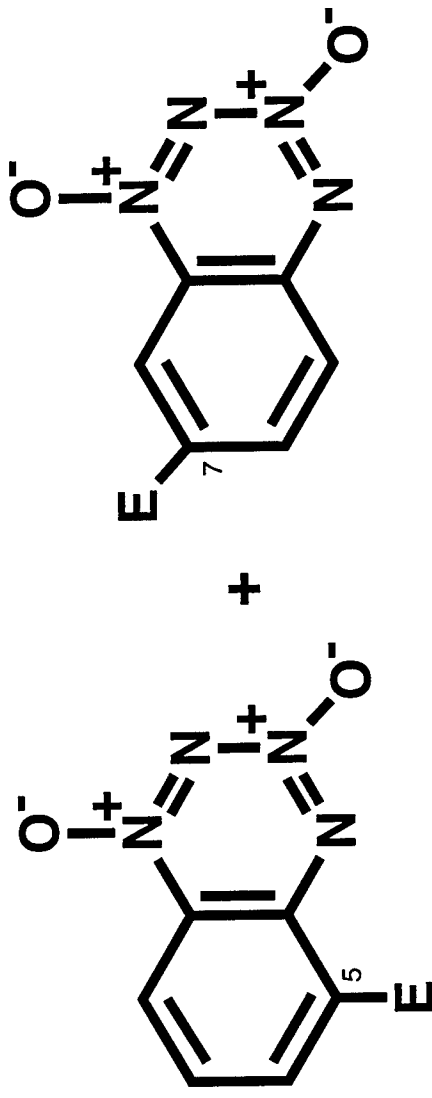
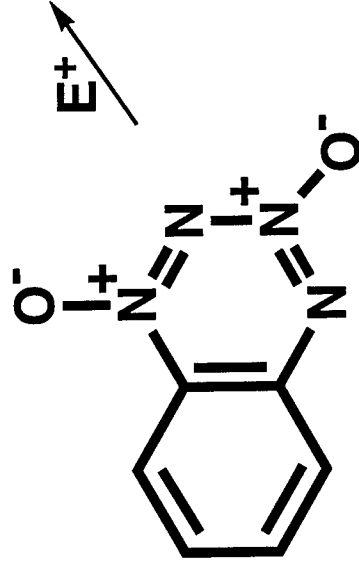


Venugopal (OSU-DARPA).

Substituted Benzotetrazine 1,3-Di-N-oxides

Electrophilic substitutions (Moscow) of benzotetrazine 1,3-di-N-oxides occur readily at 5- and 7- positions.

The C₅- and C₇- substituted benzotetrazine 1,3-di-N-oxides undergo rapid displacements by hard nucleophiles. Very important!

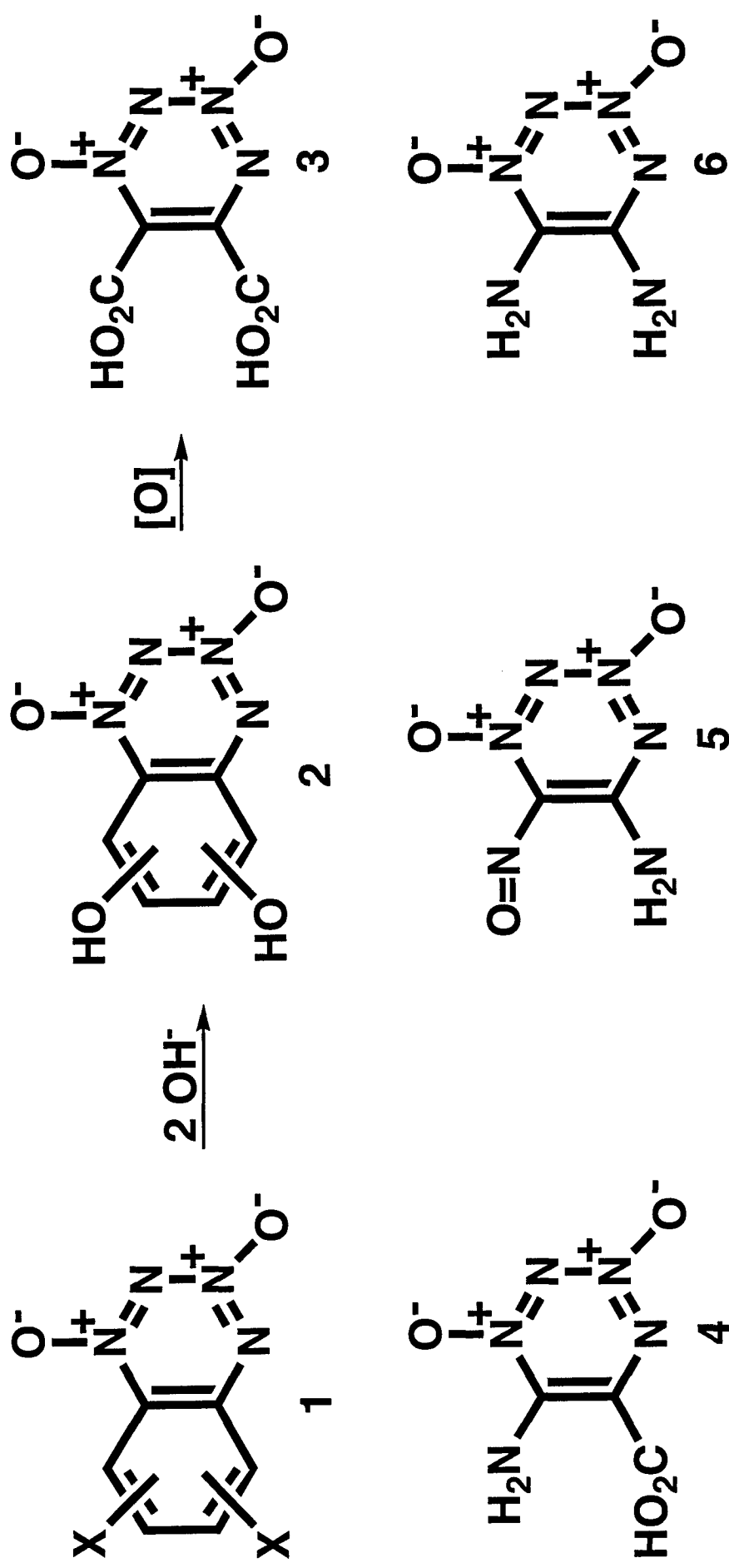


Nuc = OH, OAc, NH₂ and OSiR₃ have not been reported by Moscow! Why not? Does the tetrazine dioxide ring open?

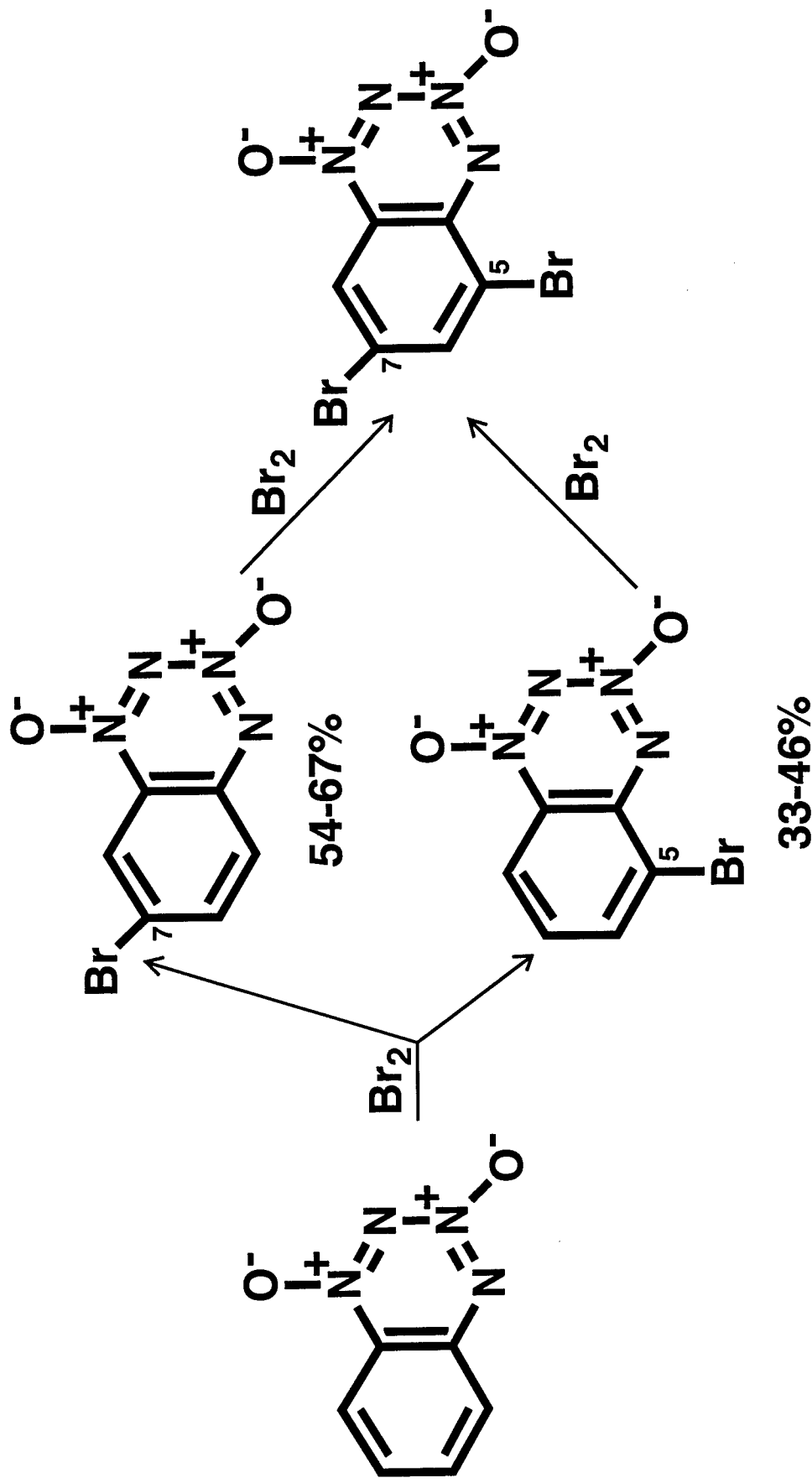


Syntheses of 1,2,3,4-Tetrazine 1,3-Di-N-oxides

The following displacements and subsequent reactions have been major present objectives (Dr. Venugopal) at OSU. Many different oxidizing agents might have to be studied in order to prepare 5,6-dicarboxytetrazine 1,3-di-N-oxide (3) from 2.

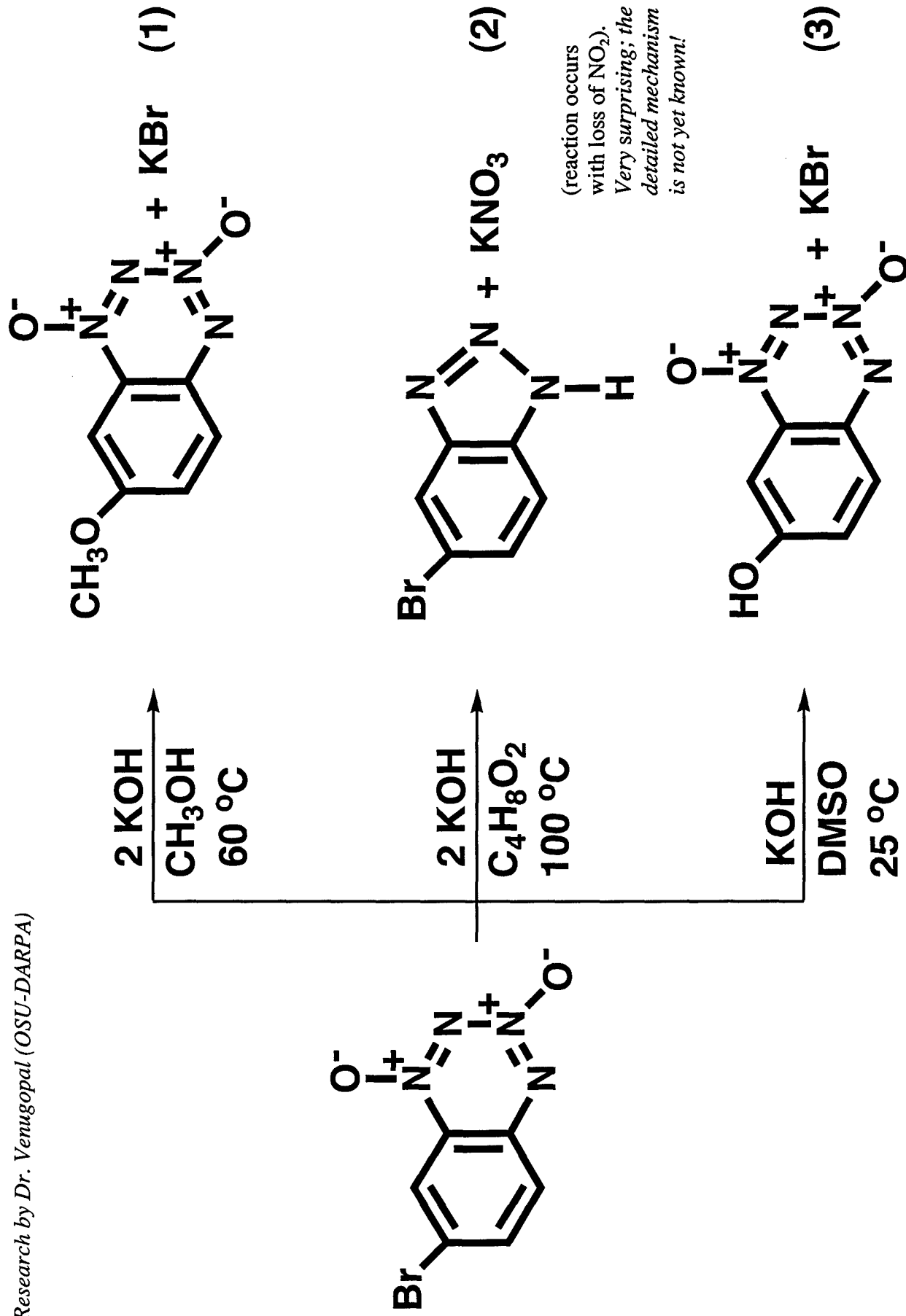


Can simple 1,2,3,4-tetrazine 1,3-di-N-oxides such as 3-6 be prepared? Are they sufficiently stable for use in syntheses of DTTO and/or IsoDTTO? The physical-organic chemistries of such compounds need determination.

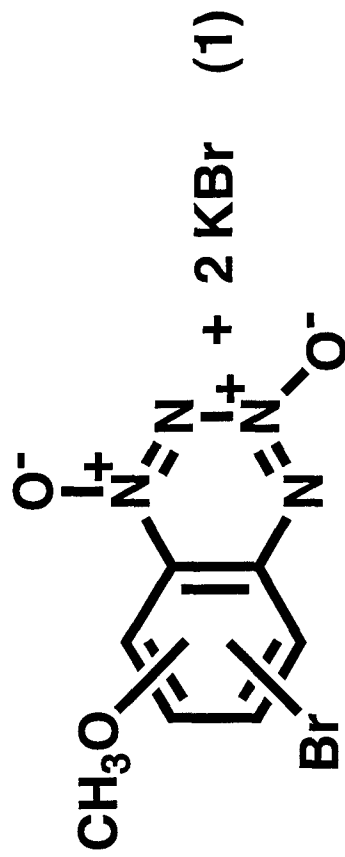


Venugopal (OSU-DARPA).

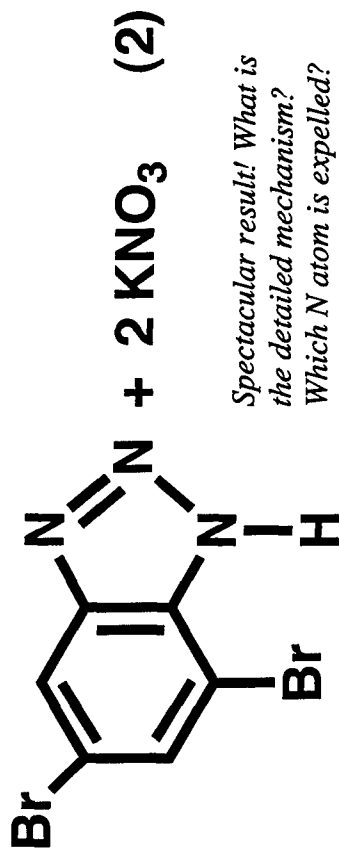
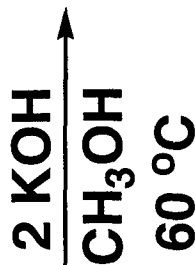
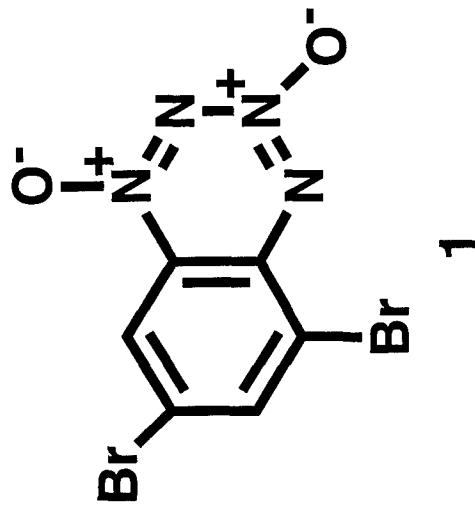
The above bromination reactions have been studied at OSU. They work well as indicated and the products are readily separated and quite stable. Present results agree with that communicated by Moscow. Of interest now are syntheses and reactions of iodobenzotetrazine 1,3-di-N-oxides! Will the iodines be very replaceable? Chlorination and fluorination?



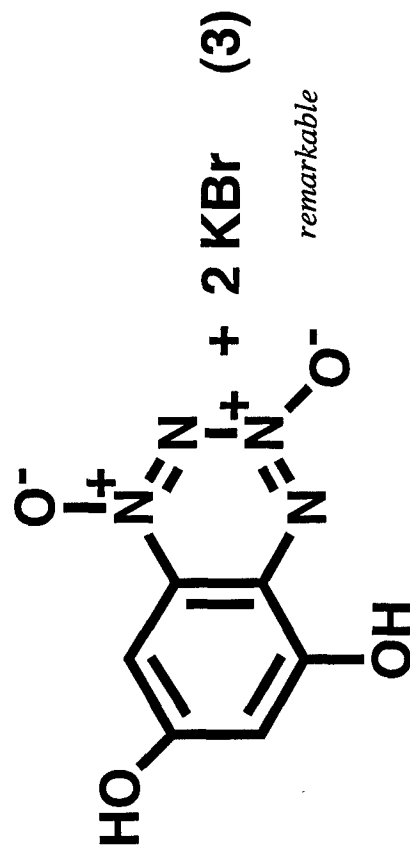
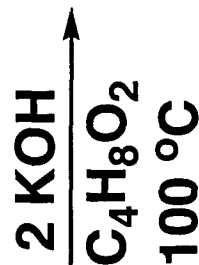
These displacement and ring-opening reactions have been studied at OSU by Dr. Venugopal. Reaction 1 occurs as expected. Reaction 2 using KOH at 100 °C occurs *surprisingly* to give the indicated triazole in good yields. Reaction 3 occurs at 25 °C. This important low temperature reaction will be studied further. These observations are very important. Moscow has not reported such reactions.



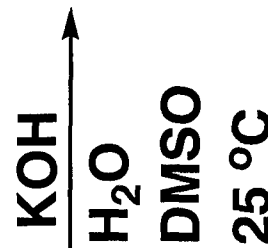
good yields, expected!



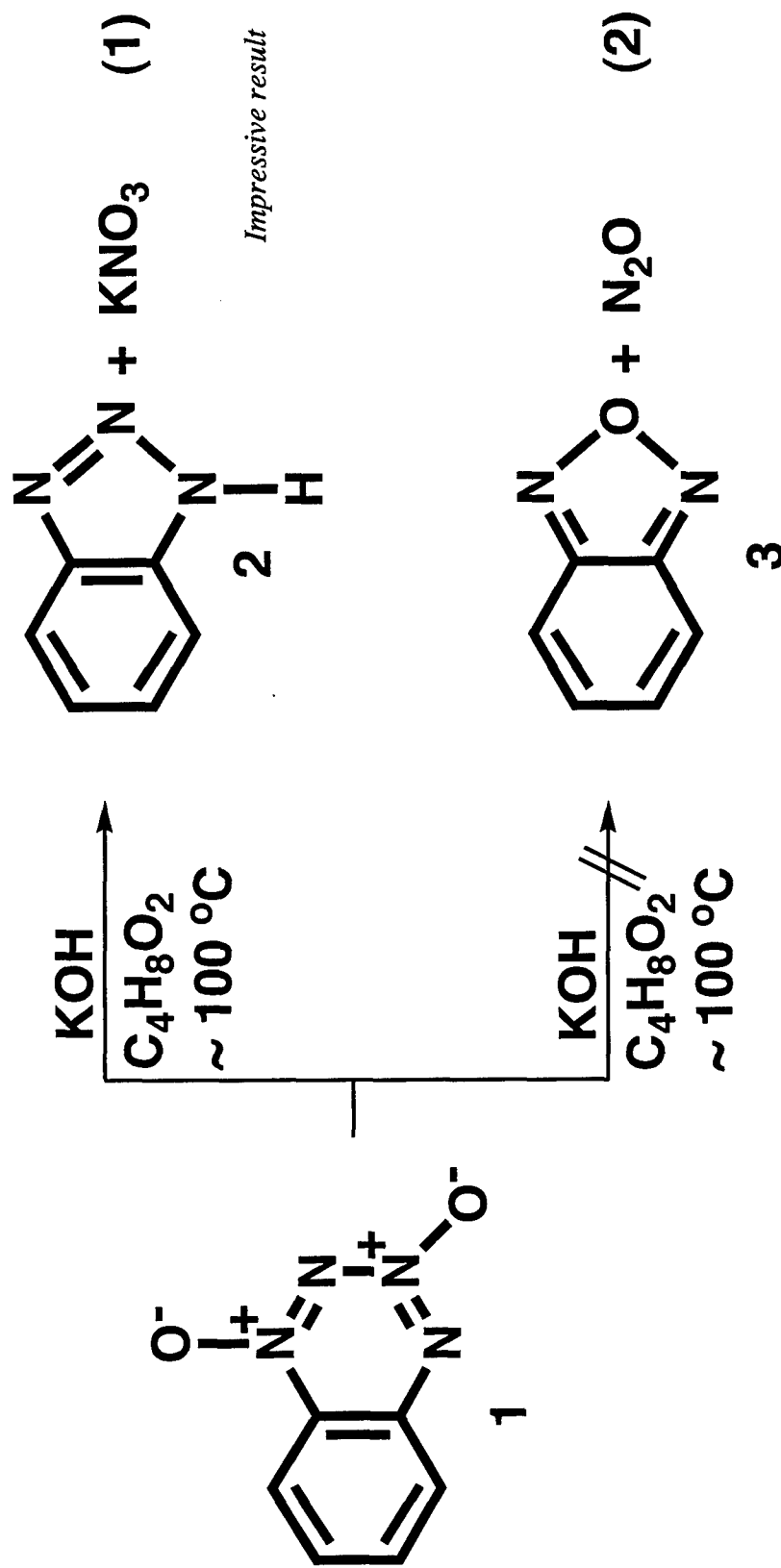
Spectacular result! What is the detailed mechanism?
Which N atom is expelled?



remarkable

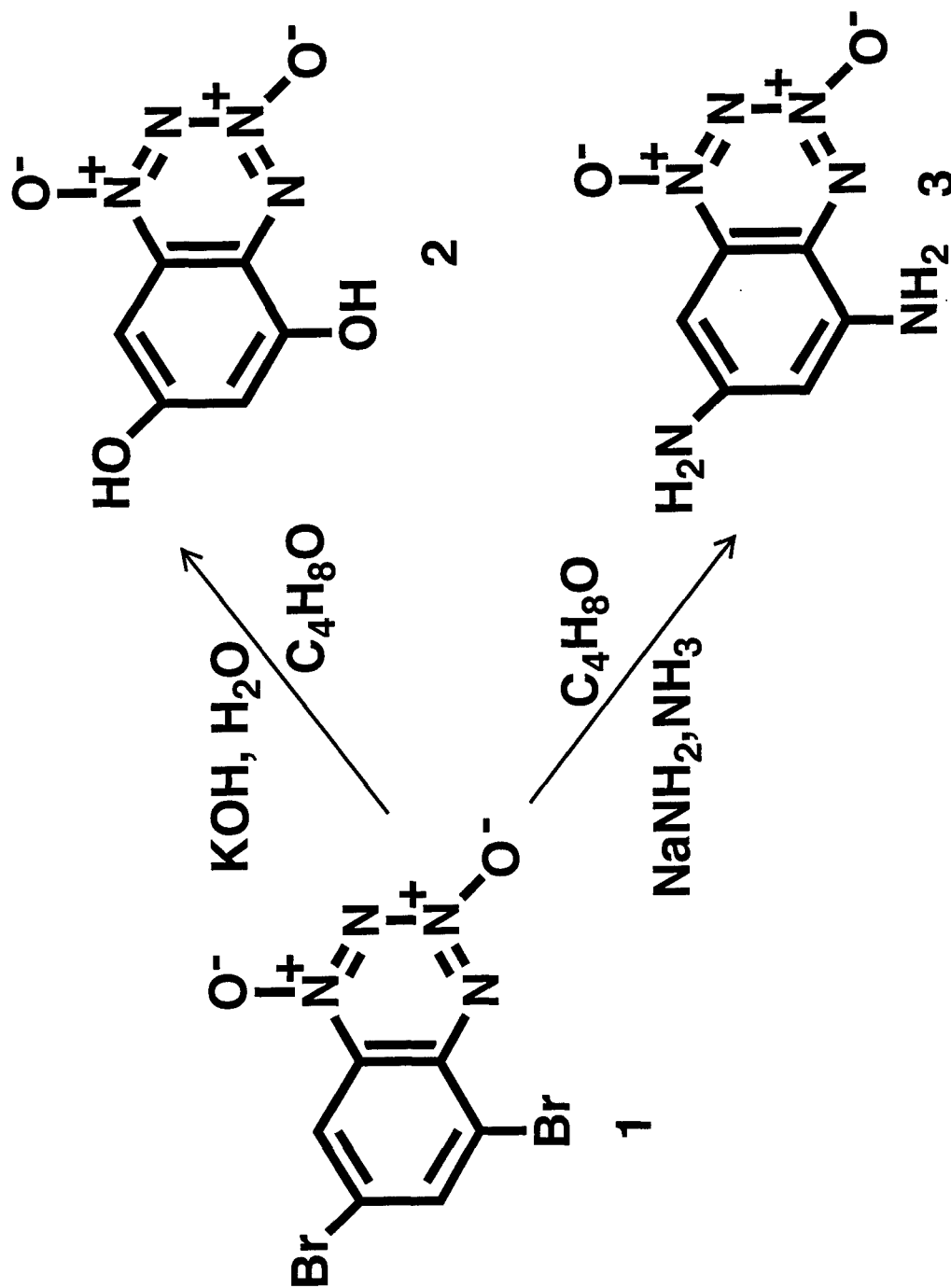


The different behaviors of 5,7-dibromobenzotetrazine 1,3-di-N-oxide (1) with CH₃O⁻ and OH⁻ ions in reactions 1 and 2 are similar to that found for 7-bromobenzotetrazine 1,3-di-N-oxide, as on page 46. The conversion of the 1,3-di-N-oxide to a triazole again is impressive! The structure of the product of displacements as in reaction 3 is tentative. Further study is necessary. Are we going to be allowed to finish this work? This is very important in the DTTO and/or IsoDTTO programs!



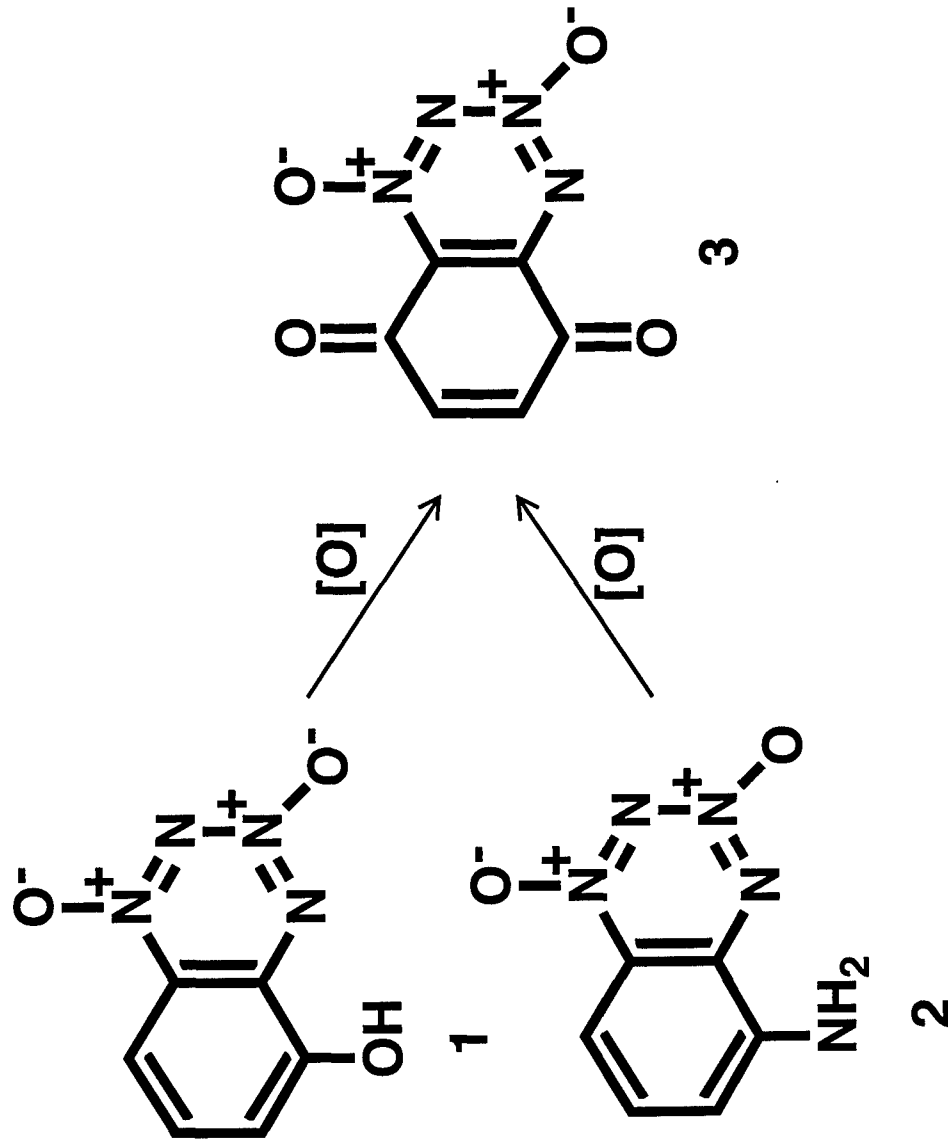
Venugopal (OSU-DARPA).

Reactions of halobenzotetrazine 1,3-di-N-oxides with hot KOH to give halobenzotriazoles as in pages 46 and 47 are unexpected! Further, benzotetrazine 1 and hot KOH yield benzotriazole (2). Benzofurazan (3) was the product expected. It is important that the hydrolytic behaviors of benzotetrazine 1,3-di-N-oxides be understandable and controllable. Many schemes for synthesis of DTTO and/or IsoDTTO have been based on the expectations that in hydrolyses of hetero 1,3-di-N-oxides, the tetrazine 1,3-di-N-oxide units will be inert. It is essential that these studies be completed. This work should not be lost to the Russians. Again, this work should be finished and published quickly! Dr. Venugopal is no longer here.



The low temperature behaviors of 1 with KOH and with NaNH_2 should be studied further in efforts to prepare 2 and 3, respectively. Tetrazines 2 and 3 are of interest for oxidative conversions to benzotetrazine-1,3-di-N-oxido-5,6-dicarboxylic acid and its derivatives. It is important in programs for synthesis of DTTO and/or IsoDTTO to know whether simple 1,2,3,4-tetrazine 1,3-di-N-oxides are stable and usable. These studies should be continued! Please allow us to present our work at government conferences.

Synthesis of Quinotetrazine 1,3-Di-N-oxides



Syntheses of 1 and (or) 2 are to be completed by controlled displacement reactions as on previous pages. Oxidations of 1 and (or) 2 to quinone 3 or otherwise should then be investigated. Can the quinone moiety be oxidized; will the simple 1,2,3,4-tetrazine 1,3-di-N-oxide ring system stay intact? These efforts relate to future practical syntheses of DTTO, IsoDTTO and other energetic materials.